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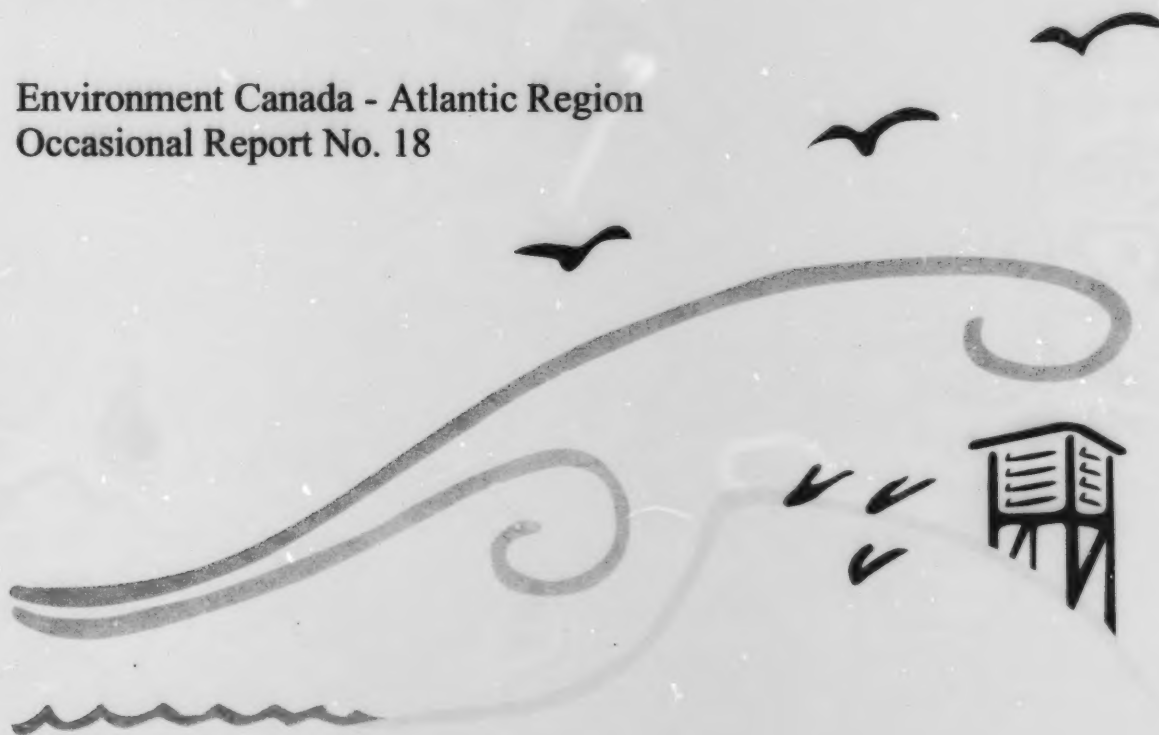
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# **Cycling of Mercury in Kejimikujik National Park**

**Toxic Substance Research Initiative  
Project # 124 Summary, December 2001**

**Edited by: Nelson O'Driscoll, Thomas Clair  
and Andy Rencz**

**Environment Canada - Atlantic Region  
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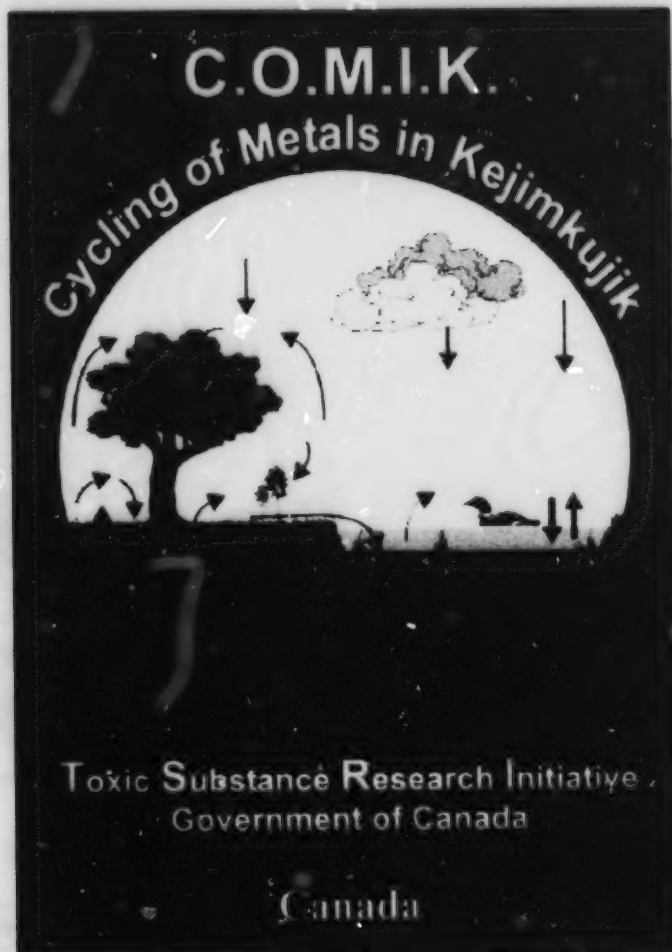
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## Preamble

The objective of this report is mainly for communication of results between the researchers (to initiate discussion of results and future directions). To date the results presented in this report have not been technically reviewed. Questions and comments are appreciated.

## Executive Summary

Much has been learned about the mercury cycle in Kejimikujik Park Nova Scotia over the past 3 years of research. This executive summary contains an outline of some of the major developments found within each section of this report.

### Lake Sediments:

Lead isotope results suggest that the upcore enrichment of mercury and lead is weakly bound in the labile phase. Lead isotope results suggest two potential geologic sources of lead but remobilization issues have not yet been resolved.

### Atmospheric:

Research has indicated that the presence of very small levels of  $\text{SO}_2$  in the atmosphere can increase the solubility of  $\text{Hg}^0$  in water by at least four orders of magnitude. Studies to date have assumed the solubility of  $\text{Hg}^0$  in lake waters to be the same as in distilled water, which now seems incorrect. It is not yet known at this time whether highly soluble  $\text{SO}_2$  forms a complex with dissolved  $\text{Hg}^0$ , or whether atmospheric (gaseous)  $\text{SO}_2$  carries  $\text{Hg}^0$  into the aqueous phase as a soluble  $\text{Hg}\cdot\text{SO}_2$  complex.

### Flux:

Mercury flux measurements over undisturbed soil and water indicate that rates are generally low in the region ( $1.2 \text{ ng m}^{-2} \text{ h}^{-1}$ ,  $n=8$ ) and are similar to the mean flux rates over clear and colored water ( $1.3 \text{ ng m}^{-2} \text{ h}^{-1}$ ;  $n=10$ ). Evasion is the dominant process with some deposition occurring at night. Relationships that were observed with physical and chemical parameters are being explored (wind, temperature, pH, soil moisture etc.). No correlations were observed between flux and amount of mercury in the substrate. Vegetative flux from a White Pine tree showed a large range from  $-17$  to  $+29 \text{ ng m}^{-2} \text{ h}^{-1}$ . This implies a significant flux from vegetation that has not been accounted for.

Lake water to air flux of mercury is dependent upon several factors including the levels of dissolved gaseous mercury (DGM) in the water column. DGM in the water column was related to microbial reduction and oxidation mechanisms that are driven by photo-produced hydrogen peroxide. A continuous analysis method for DGM and water chemistry was developed that can be used on remote lake sites. This method is being used to examine the interactions between DGM, water chemistry, meteorology, and flux.

### Surface Water (Lakes and Streams) Chemistry Surveys:

These indicated that mercury ranges from  $0.5 \text{ ng L}^{-1}$  to a maximum of  $27.7 \text{ ng L}^{-1}$  and dissolved organic carbon (DOC) values from  $1 \text{ mg L}^{-1}$  to  $91 \text{ mg L}^{-1}$  with a strong positive

correlation between Hg and DOC. The pH values of waters in the area sampled vary from 3.5 to 7 with most ranging between 4 and 5.25. The results did not seem to indicate a significant bedrock source of sulphate; however buffering capacity is limited. A large number of the high mercury samples were found near possible geologic sources of mercury (black sulphidic slates of the Halifax Formation, biotite rich granites and faults in the park) but no firm link has yet been established between geology and high mercury in water. It is suggested that this control on the Hg and DOC anomalism results from favorable conditions for bog formation over the poorly drained black slates.

#### Groundwater:

While limited groundwater analysis was performed, it indicated there was significant groundwater mercury inflow into Big Dam West Lake (high of  $4.26 \text{ mL min}^{-1}$  in June). Total Hg ranged between  $0.7 - 6.5 \text{ ng L}^{-1}$ , with a mean of  $2.98 \text{ ng L}^{-1}$ . Similar results were obtained for July (average inflow  $= 1.83 \text{ mL min}^{-1}$ , average Hg  $= 0.825 \text{ ng L}^{-1}$ ). Values were extrapolated to the rest of the year (assumed May flow would be similar to June and October was used to provide average values for November to April) to calculate fluxes. Preliminary calculations indicate that 52 g of mercury are transported by groundwater into BDW each year. Methyl mercury results are pending.

#### Geology:

Geological surveys within the park indicate that samples from surface exposures in the Park area contain very low mercury levels. Mercury is lowest in rocks of the Goldenville Formation and Kejimikujik Monzogranite, varying from  $<0.5 \text{ ng g}^{-1}$  to  $4.0 \text{ ng g}^{-1}$  ( $n=47$ ) and  $<0.5$  to  $5.8 \text{ ng g}^{-1}$  ( $n=31$ ) respectively. Halifax slate samples are marginally higher at  $<0.5$  to  $16.4 \text{ ng g}^{-1}$  ( $n=100$ ). Samples of Goldenville and Halifax Formation lithologies from drill core contain substantially higher concentrations of Hg (from  $<0.5$  to  $242 \text{ ng g}^{-1}$ ). Some of the highest Hg analyses are related to traces of sphalerite  $[(\text{Zn},\text{Fe})\text{S}]$ . The data may indicate that there is an incipient devolatilization of Hg from the bedrock surface during the earliest phases of weathering, thereby releasing Hg to soils, vegetation, water, and the atmosphere. The effect is most pronounced in sulphidic black slates, which are more porous, have a well developed cleavage, and have an inherent acid generation capacity with the presence of up to 5 percent pyrite and pyrrhotite.

#### Soils:

Techniques for the sequential extractions of mercury in of soils were developed. Initial application of a 5-step procedure to humus and A-horizon soils indicated that the percentage of organically bound Hg (extracted with pyrophosphate) in humus was surprisingly small ( $<20\%$ ) and significantly less than that in the A-horizon samples, though the absolute amount of this organically bound Hg in humus was greater. This unanticipated result led to more research into the wet chemical scheme, specifically to the development and optimisation of a nitric acid step prior to the final aqua regia digestion that would dissolve all remaining non-sulphide bound mercury. The new 6-step procedure then showed that the 'missing' organically bound mercury in humus was dissolved by this  $\text{HNO}_3$  digestion, indicating that this form of mercury was held with the humin fraction, the non-labile form of organically bound mercury. This development is significant in that it indicates conventional application of common extraction schemes

leads to erroneous results. The analytical research was again extended to verify where other forms of mercury were dissolving in the sequence. These forms include synthetically derived Hg, Hg<sub>2</sub>Cl<sub>2</sub>, HgCl<sub>2</sub>, HgO, HgS, and HgS (cinnabar), which were mixed intimately and homogeneously in granite and subjected to the schemes. The results also indicate that previous extraction schemes are in error since the stability of Hg is an issue and is usually overlooked, causing incorrect interpretations and conclusions.

Mercury in soil gas was surveyed using a silver strip adsorption method. The minimum reported Hg in soil gas value is 0 ng Hg / strip and the maximum value is 78 ng Hg / strip (n = 94, mean = 4.7 ng, s.d. = 9.3 ng). Values for this study range from 0.6 ng Hg / strip and values 37 ng Hg / strip are considered anomalous. Apart from two highly anomalous values (46 and 78 ng Hg / strip) all values range between 0-15 ng Hg / strip. The data indicate there is a strong spatial relationship between inferred structures, namely the Tobiatic Shear Zone, and anomalous Hg in the overlying soil gas. There also appears to be a positive relationship between Au mineralization in the West Caledonia Gold District and anomalous Hg in soil gas.

#### Spatial Analysis:

GIS applications within the group have included the calculation of net mercury uptake in vegetation and the relation between mercury, methyl mercury and DOC in lakes and streams. The results indicate that the amount of total mercury in NPP (terrestrial vegetation) within the BDW drainage basin ranges from 3 mg m<sup>-2</sup> yr<sup>-1</sup> to 5.2 mg m<sup>-2</sup> yr<sup>-1</sup>. Over the entire basin the uptake in vegetation is 123 g year<sup>-1</sup>.

A GIS analysis of water data indicated that there is a very close statistical relationship between total mercury and methyl mercury in the Park waters in the summer, but not in early spring surface waters. Methyl mercury is approximately 10 % of the total. There is also a close relationship between dissolved organic carbon and total Hg in both summer and early spring. However, there is a relationship between methyl Hg and DOC only for the summer sampling and not for the spring. A predictive model is being developed.

Remote sensing was used to examine the spectral reflectance of lake in relation to DOC content. It was determined that it is possible to use spectral readings to predict the level of DOC in lakes from Kejimikujik Park. A predictive equation for DOC was also developed based on basin characteristics. Three variables, flushing rate, area of deciduous forest and area of open land within the watershed, were included in the equation. All three variables were found to be important factors controlling the amount of DOC present within the lake through the identification of positive correlations.

#### Analytical Issues:

Improvements in analytical methodology have been a concern throughout this project. Through intensive studies it was determined that the stability of Hg in water without an added preservative (BrCl) depends upon the amount of DOC present. It was also shown that inexpensive high density polyethylene (HDPE) or polypropylene (PP) bottles can be used for water sampling without danger of contamination from either the bottle or the atmosphere on storage.

**Mass Balance Development:**

A mass balance model is currently under development but the preliminary results indicate that we are missing 140 g of mercury inputs to the Big Dam West Lake basin using the current calculations. We are currently working to identify the source of the discrepancy.

## 1. General Introduction

*N.J. O'Driscoll, D. Lean, and A. Rencz*

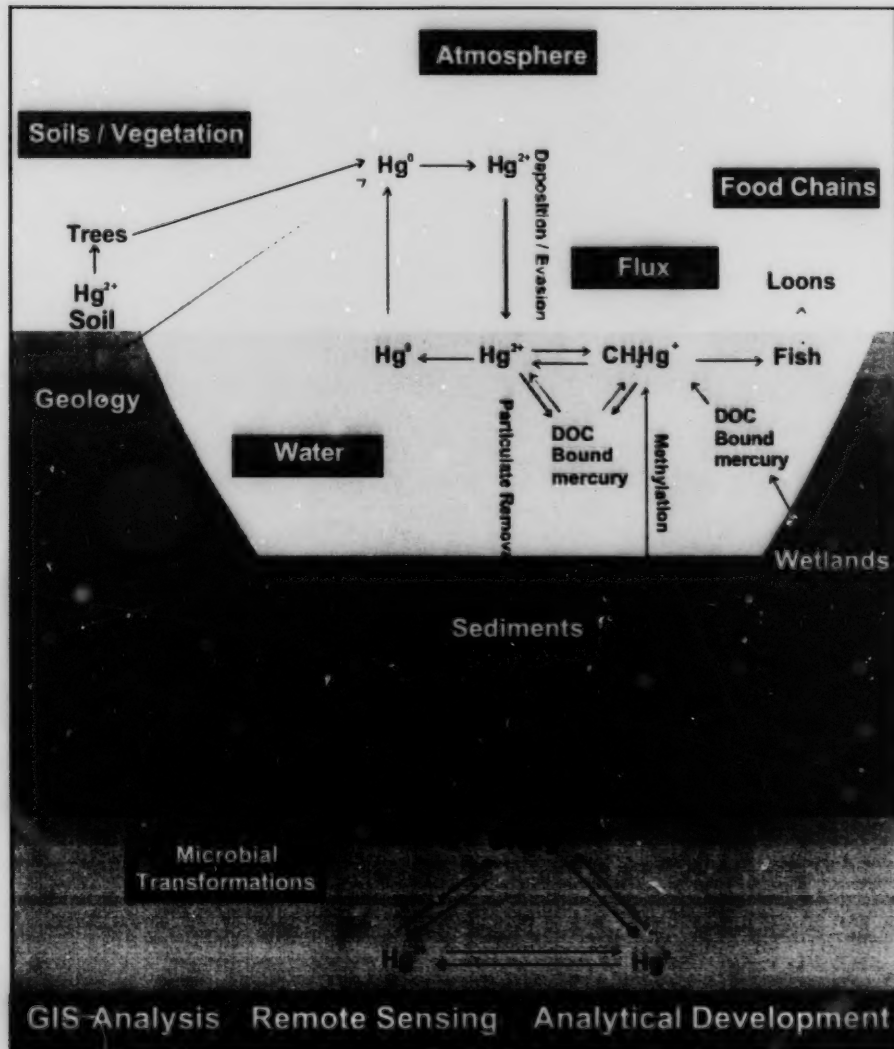


**Figure 1-1:** The ecosystem components and supporting research areas of the mercury cycle in Kejimikujik Park

This report is the mid-year summary of mercury research (TSRI research group #124) in Kejimikujik Park, Nova Scotia March 1999 – March 2002. This document begins with a general introduction to mercury cycling and a review of some of the relevant literature, followed by the individual project reports. The reports are organized according to the ecosystem components of Kejimikujik as outlined in Figure 1-1. The various sections also comprise the focused areas of mass balance studies currently underway.

### Mercury Cycling in Ecosystems

Problems associated with mercury pollution have been reported globally for quite some time. Mercury pollution first received worldwide attention with the Minimata Bay disaster in Japan in 1953, when large numbers of fisherman working in the waters near the Chisso Chemical Company began to be diagnosed with neurological disorders. It was subsequently determined that the company was releasing inorganic (366 ppm) and methyl mercury (140 ppm) to the waters of Minimata Bay as a by-product of acetaldehyde production (Government of Ontario, 1976). The methyl mercury (MeHg) bioaccumulated in shellfish and was in turn passed on to the humans who were consuming it. By October of 1975 ninety people in Minimata had died due to methyl mercury poisoning.

Mercury poisoning in humans is a widespread phenomenon not restricted to environmental disasters like Minimata. In 1997 the USEPA found that 1-3 % of U.S. women of childbearing age come into contact with harmful mercury concentrations through the consumption of fish. Although MeHg comprises on average between 1-10 % of the total Hg present in freshwater, it amounts to 90% of the total found in fish (Holden, 1973; Driscoll et al., 1994; Becker & Bigham, 1995). Methyl mercury has been found to bioaccumulate by a factor of between 10,000 and 500,000 for predatory fish and marine mammals (W.H.O., 1990; Leonard et al., 1995). Communities with high fish consumption rates are therefore at high risk of MeHg poisoning. The current Ontario guidelines state that mercury in fish tissue over a concentration of 0.5 :g / g dry weight is unsuitable to eat. The human intake of MeHg occurs primarily via ingestion and gastrointestinal absorption. Because MeHg is soluble in fats, the percent absorbed is close to 100% (Fergusson, 1990). Methyl mercury elimination in humans and lab animals can be expressed as a single half-time since the excretion rate is directly proportional to the body burden (WHO, 1990). Whole body half times have been seen to range between 52-93 days with an average of 70 days (WHO, 1990). Methyl mercury poisoning will produce detrimental effects on both the physiological and neurological systems in the human body. Methyl mercury is capable of damaging the central nervous system due to its ability to pass the blood-brain barrier and destroy brain cells (Annau & Eccles, 1987, Fergusson, 1990).

While methyl mercury is the main form of mercury that bioaccumulates, there are several forms of mercury present in the environment that can transform and have an effect on the production of methyl mercury in an ecosystem. There are three major mercury species, each of which are critical to the cycling of mercury on a global basis and are ubiquitous. The main form of mercury in the atmosphere, is elemental mercury ( $Hg^0$ ) (due to its volatility), while the predominant form in water is inorganic mercury ( $Hg^{2+}$ ), bound to

various organic and inorganic ligands. The predominant form of mercury in the food chain is methyl mercury ( $\text{CH}_3\text{Hg}^+$ ), because of its ability to bioaccumulate and biomagnify. Methyl mercury can bioaccumulate and biomagnify in watersheds such that very low methyl mercury levels in water results in mercury toxicity at higher trophic levels (Morel et al., 1998, Eccles and Annau, 1987).

### **Mercury Research in Kejimikujik Park**

Kejimikujik National Park is located near the western peninsula of Nova Scotia, Canada (Canada map sheet 21 A/6) in a relatively flat topographic area (Figure 1-2). The park has been the site of many acid rain studies, and more recently many mercury cycling studies as well (Beauchamp et al., 1998, Beattie & Whelpdale, 1989, Delorme et al., 1984). It has been found in recent years that the concentrations of mercury in biota (particularly loons) within the park are quite high. Concentrations of mercury in Kejimikujik loon blood (6 – 7 :g Hg /g) are higher than most other areas in North America (1-3 :g Hg /g), and this has resulted in negative impacts on loon reproduction and behaviour (Evers et al., 1998; Burgess et al., 1998). Studies indicate that within Kejimikujik Park loons with a mercury concentration in blood <2.5 :g/g will fledge 1 chick/ mating pair, while those with mercury concentrations >6.0 :g/g will fledge only 0.2 chicks / mating pair (Burgess et al., 1998).

Several reasons have been postulated for the mercury bioaccumulation problem in Kejimikujik Park. One variable that is currently under debate is the primary source of mercury to the environment. Mercury can enter the biogeochemical cycle from both natural and anthropogenic sources. Sources of mercury to Kejimikujik Park may include both anthropogenic and natural inputs from atmospheric deposition, as well as inputs derived from the underlying geology of the park (bedrock and soil). Determining the relative contributions of these sources is an important step in understanding the unique characteristics of the mercury cycle in Kejimikujik.

Another of the possible reasons for the mercury bioaccumulation problem is the unique physical and chemical environment of the park ecosystem. In general the Kejimikujik lakes and streams are characterized by high dissolved organic carbon content, low pH (4.2 to 5.5), high percentage wetlands in the catchments, and slow fish growth (Kerekes & Freedman, 1989, Howell, 1989). Each of these factors has been shown to result in high fish mercury concentrations. This paper will explore the interrelationship of these factors and their affect on the mercury cycle, in order to help explain the situation observed in Kejimikujik Park, Nova Scotia.



**Figure 1-2: Location of Kejimikujik Park, Nova Scotia**

#### **Atmospheric Sources of Mercury**

In contrast to the mercury bioaccumulation disaster that occurred in Minimata, Japan, Kejimikujik Park has no direct industrial inputs of mercury. There are however, naturally occurring sources of mercury within the park. Mercury can enter a watershed from several different primary sources; the most commonly cited source is atmospheric deposition. The global atmospheric mercury pool is currently estimated to be approximately  $5 \times 10^9$  g (Fitzgerald, 1994). This mercury does not remain in the atmosphere; it is constantly being converted into more soluble forms and being deposited in water bodies. Therefore the atmospheric emissions of mercury have a direct link to the cycling of mercury in watersheds. Current research using techniques such as peat bog cores as metal deposition archives indicates that mean amounts of total mercury in the atmosphere have been increasing over the past 100 years (Fitzgerald, 1995; Martinez-Cortizas et al., 1999). Fitzgerald (1995) has suggested that mercury concentrations have been increasing at a rate of 0.6 % over the past century, while Watras and Huckabee (1994) have found the increase to be closer to 1 % per year. Several recent studies also indicated that these increases could not be accounted for by geologic sources and that human-related mercury emissions since the industrial revolution are the cause of elevated mercury concentrations in the atmosphere (Fitzgerald et al., 1998; Heyvaert et al., 2000). It has been observed using lead isotope dating of a sectioned peat core that mercury

concentrations in a peat bog within Kejimikujik Park peaked in the early 1970's with recent increases in 1992 (Burgess et al., 1998). Kejimikujik Park is located downwind of North American anthropogenic pollution sources that may contribute mercury to the atmosphere.

These studies suggest that increasing concentrations of mercury in the atmosphere may play a significant role in the mercury bioaccumulation problem. However, the Kejimikujik ecosystem does not receive mercury inputs greater than that commonly received in other ecosystems. For example, the average mercury concentration in air over Kejimikujik ranges from 0.51 to 2.9 ng/m<sup>3</sup> with a mean annual concentration of 1.52 ng/m<sup>3</sup> (Beauchamp et al., 1997). It was also found that the mean 6-month average of mercury in precipitation for 1996 was 11.4 ng/L. These results are within the range of other North American mercury deposition sites (EPA, 1997), and indicate that the atmosphere is not the most predominant factor in mercury bioaccumulation in the Kejimikujik ecosystem.

#### **Geologic Sources of Mercury**

Another possible source of mercury to the Kejimikujik ecosystem is the presence of mercury containing bedrock geology within the park. The Meguma bedrock group is found in Nova Scotia and adjacent offshore areas. The Meguma group is known as the "Gold Bearing Series", and may contain high mercury concentrations due to the common formation of a mercury-gold amalgam. The group is traditionally divided into the upper shaly unit (Halifax Formation) and the lower sandy unit (Goldenville Formation). Slates of the Halifax formation underlay the eastern portion of Kejimikujik Park. The bedrock in this area is covered by glacial debris that has been shaped into drumlins numbering approximately 200 (Cumming, 1985). The major granite rock unit is found in the southwestern portion of the park and a smaller section of Goldenville greywacke is found just to the east of this.

Preliminary data from bedrock sampling within Kejimikujik Park indicates that the mercury content of the geology (0.2 ng/g to 38.9 ng/g for surface outcrop) is generally within the range of other areas within Canada, with the exception of a few high concentration areas (>200 ng/g) found within the park (O'Driscoll et al., 2000, Cumming, 1985). This data indicates that mercury concentrations in bedrock geology is not an unusual factor contributing to the mercury bioaccumulation problem in Kejimikujik Park. The distribution of mercury containing geologic formations within Kejimikujik park (relative to the rest of Canada), is however, a factor in determining the mercury concentrations found within the ecosystem.

#### **Within-Lake Mercury Loss Processes**

Since Kejimikujik Park does not seem to be the recipient of any unusual sources of mercury, a better understanding of the factors that lead to the bioaccumulation of mercury may be found by examining the internal mercury cycling processes in the park and the factors that affect them. Studies of mercury loss processes in a water column are important as they determine the residence time of total mercury within a water column.

concentrations in a peat bog within Kejimikujik Park peaked in the early 1970's with recent increases in 1992 (Burgess et al., 1998). Kejimikujik Park is located downwind of North American anthropogenic pollution sources that may contribute mercury to the atmosphere.

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more MeHg per unit area to water downstream than areas that contain no wetlands (Rudd, 1995). Similar findings in Sweden, Wisconsin, and the Adirondack lakes have shown the importance of wetlands as a MeHg source (Krabbenhoft et al., 1995; Driscoll et al., 1994). Rudd (1995) estimates that the MeHg production from wetlands surrounding the catchments studied must equal at least  $4.4 \text{ mg ha}^{-1} \text{ yr}^{-1}$  to support the amount of MeHg exported.

Several studies have indicated correlations between DOC and MeHg transport. Krabbenhoft et al. (1995) observed that the Allequash creek wetland in Northern Wisconsin released a substantial amount of DOC to a stream in fall. It was also observed that there was a two-fold increase in Hg concentrations in the stream; however, no effects were observed on MeHg concentrations. Pettersson et al. (1995) found that the amount of MeHg associated with humic substances taken from a mire in Northern Sweden increased with increasing concentrations of humic substances. Lee and Hultberg (1990) studied runoff from a catchment in the Lake Gardsjon watershed, where it was determined that MeHg was associated with humic substances and that they are transported together from the catchment by runoff to lake water. O'Driscoll and Evans (2000) observed that substantial amounts of methyl mercury can bind to DOC which thereby serves as a transporting agent from wetlands.

While much research has been published on the relationship between DOC and mercury, there is much left to learn. The EPA report to Congress (1997) identified several of the gaps in mercury fate and transport modelling. It was noted that a better understanding of mercury transport from watershed to water body was needed. The report also states that it is particularly important that mercury measurements that are presently operationally defined (e.g. "adsorbed to organic material") be made in such a way that mercury residues in fish can be correlated with the bioavailable mercury pool.

#### **The Role of the Food Chain in Mercury Cycling**

Since methyl mercury can biomagnify in a food chain, the amount of mercury an organism will contain is directly related to the trophic position of that organism (Zanden and Rasmussen, 1996). The loons of Kejimikujik Park are at the top of the aquatic food chain and therefore have high mercury concentrations. Food sources for the loons in Kejimikujik include fish such as the yellow perch. It has been shown that yellow perch in Kejimikujik Lakes grow slowly and contain high amounts of mercury (Burgess et al., 1998, O'Driscoll et al., 2000). This may be due to food chain effects. Acid stressed lakes such as Kejimikujik tend to have low numbers of benthos in the lake sediment. Without this food source perch may be unable to grow large enough to eat small fish and therefore make up their diet with phytoplankton and macrophyta. More food is ingested to balance the energy expended in obtaining the food, and therefore more mercury is accumulated. Since the fish are growing slowly there is also no growth dilution effect to counter the increased mercury load.

### Summary

The primary sources of mercury to Kejimikujik Park (atmospheric deposition and bedrock geology) are not unusually different from those in other areas of North America. The reason for the bioaccumulation of mercury within the park must therefore be related to internal ecosystem characteristics that affect the cycling and speciation of mercury. The lakes within Kejimikujik Park have many characteristics that have been shown in the literature to result in increased mercury accumulation in the food chain. These include such factors as high percentage wetlands in the catchment basin, high DOC in the water column, low pH, and low productivity within the lake. An integrated and multidisciplinary study of these factors and the relationships between them is necessary to determine their relative importance to the mercury cycle within Kejimikujik watersheds.

## **Project Reports**

### **2. Lake Sediments**

#### **2.1 Mercury and Lead Isotope Analysis**

*K. Telmer and M. Watson*

##### **Objective**

- Lake sediment and pore water samples obtained from Big Dam West Lake and Big Dam East Lake are the foundation of this project and the results shown below represent the collected data to date. The full database will be complete by December 2001. The following results are based both on new data coming from present analyses and on data obtained from cores taken in a regional study of Kejimikujik National Park by the Geological Survey of Canada in 1998.

##### **Methods**

- To correctly interpret and correlate the distribution of Hg and Pb with depth from different lakes, age constraints on sediment cores were determined by Pb<sup>210</sup> dating. Assuming that the Hg concentrations at the sediment-water interface represent present deposition levels (in other words, assuming no diagenetic remobilization of Hg to the sediment-water interface), the sedimentation rate can be used to estimate total annual Hg deposition rates.
- Sediment samples, obtained from cores and sectioned in detail, are sequentially leached to extract Hg and Pb (as well as other elements). The metals are leached from two separate phases (1) weakly adsorbed and (2) resistant material such as organic compounds and silicate minerals.
- The isotopic Pb composition of each sediment extraction is determined using inductively coupled plasma mass spectrometry (ICP-MS) and solid source thermal ion mass spectrometry (TIMS). The isotopic signal provides a fingerprint for the source of Pb and by correlation other pollutants as well, while the sequential extractions ensure the purity of the fingerprint, i.e. that mineralogical Pb signals are not mixed with that adsorbed.
- To better constrain the atmospheric contribution of Pb, direct measurement of the isotopic composition of atmospheric fallout is being determined in precipitation and atmospheric particulates (dry deposition) within Kejimikujik Park with the help of Steve Beauchamp of Environment Canada. Once the source of atmospheric Pb is constrained as dominantly American or Canadian we will apply this knowledge to sourcing Hg.

- High-resolution seismic reflection data was obtained for Big Dam West Lake and Big Dam East Lake. A zigzag course over the lakes produced a 3D picture of the sediment morphology of each lake. In order to calibrate or ground-truth the seismic reflectance data, long cores, nearly reaching the glacial sediments which pre-date the lakes, were taken using a percussion coring system. Coring, together with pore water sampling and lake water sampling, will tie the acoustic data to lake biogeochemistry. For example, the acoustic data will provide a better estimate of lake sediment volume and together with sediment and pore water chemistry will provide estimates of the total amounts of Hg and Pb stored in the sediments of each of these lakes over a time scale of roughly 10,000 years. This will allow us to place constraints on some components of the local and global Hg cycle before the industrial revolution for purposes of comparison to the modern observations – i.e. how strongly have we accelerated this cycle?
- In order to use concentration and Pb isotope profiles in lake sediments to determine source apportionment and study their cycles in these lake systems, it must be determined if diagenetic remobilization of sediment-bound Hg and Pb occurs during early diagenesis of sediments. This remobilization could have the consequence of increased metal content in the upper layers of sediment, thus producing metal concentration profiles that closely resemble the increases in heavy metal inputs due to anthropogenic activities. In-situ porewater sampling provides a means to measure the diagenetic release of Hg and Pb, as well as other important diagenetic properties such as redox, DO, and pH. To measure upward porewater advection, as well as diffusion, a number of in-situ porewater samplers were spiked with Hg and Pb isotope tracers at ambient porewater concentrations.

## Results

- Depth profiles show upcore enrichment trends of Hg and Pb with concentrations as high as 300 ppb and 50 ppm, respectively, occurring at the sediment water interface (Figure 2-1). This is a typical upcore profile for many Canadian Lakes but is more difficult to explain in the Keji Park system as sediments are re-suspended by storm conditions in these shallow lakes.
- Sedimentation rates for Big Dam West Lake and Big Dam East Lake are estimated from  $Pb^{210}$  dates to be 0.92 cm/yr and 1.21 cm/yr, respectively. For Big Dam West Lake and Big Dam East Lake, the estimates of total Hg deposition rates are 37.2 g/yr and 35.6 g/yr or 2.48 and 2.37 ng/cm<sup>2</sup>/yr, respectively. This is higher than the observed atmospheric deposition to the lakes (Beauchamp, 2001, TSRI report) and necessitates a watershed input to balance.
- Results of the sequential leaching for Pb show that the upcore enrichment trends exist in the labile, or weakly adsorbed, phases digested by weak acid (Figure 2-2). Hg results are still in preparation.
- Results of isotopic ratios from the sequential extraction of a Big Dam West core give a clear indication of two sources of Pb (Figure 2-3 and 2-4): (1) a Paleozoic source

which matches the age of local geology (South Mountain Batholith) and can therefore be explained by simple local inputs, and (2) a geologically older, exotic source of Proterozoic or Archean age Pb which likely represents airborne long-range transport of particulate Pb. This "less radiogenic" or "older" Pb source (i.e. lower 208/204 and 206/204) must come from an ore body and therefore represents a pollutive industrial source. It cannot represent undifferentiated crustal material (crustal rocks of any age) that must have an isotopic signal similar to or "younger" than the signal seen for the South Mountain Batholith. In this light, it is certain that the less radiogenic source is pollution from anthropogenic sources such as mining, industry, and gasoline additives. What remains to be resolved is what portion of this pollution signal is Canadian versus American. However, the less radiogenic "older" signal in the more recent sediments strongly points towards a Canadian source as American sources dominantly come from younger Phanerozoic rocks such as the classical Mississippi Valley-type Pb-Zn deposits of Paleozoic age. Complicating this scenario is the fact that sources of Pb appear to vary with depth in sediments (Figure 2-4). However, the issue of remobilization has not yet been resolved and may be an important factor. This is being addressed by ongoing porewater analyses.

- The pore water results (Figure 2-5) show that nearly all of the dissolved oxygen is utilized in the top 3 cm and that anoxic conditions occur below this depth. It can also be seen that pH steadily increases with sediment depth from a pH of approximately 4.7 at the sediment surface to pH 6.0 at depth. This may be explained by increases in bicarbonate production from the diagenetic decomposition of organic matter.
- Preliminary results found that the Pb in pore waters increased with depth (Figure 2-6). Such profiles may suggest that the diagenetic dissolution of Pb is occurring at depth and therefore could be an upward conveyor of Pb to the sediment-water interface.
- The analysis of pore water samplers spiked with isotope tracers over the duration of 21 days is being measured by ICP-MS and are anticipated to provide strong critical evidence for constraining the upward mobilization of Hg and Pb in lake sediments.

Figure 2-1

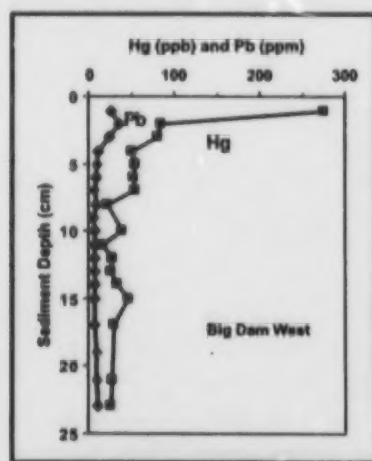


Figure 2-2

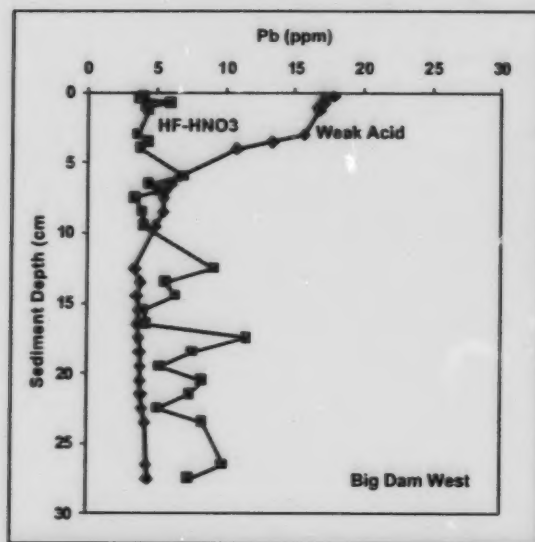


Figure 2-3

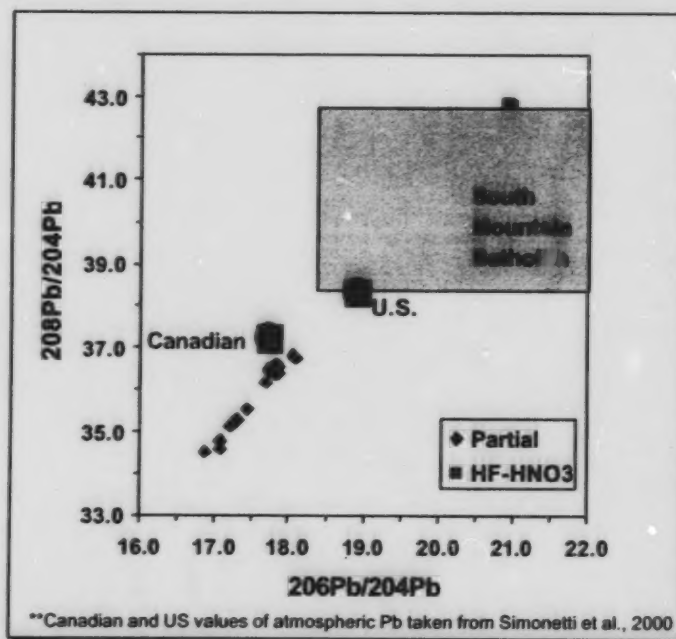


Figure 2-4

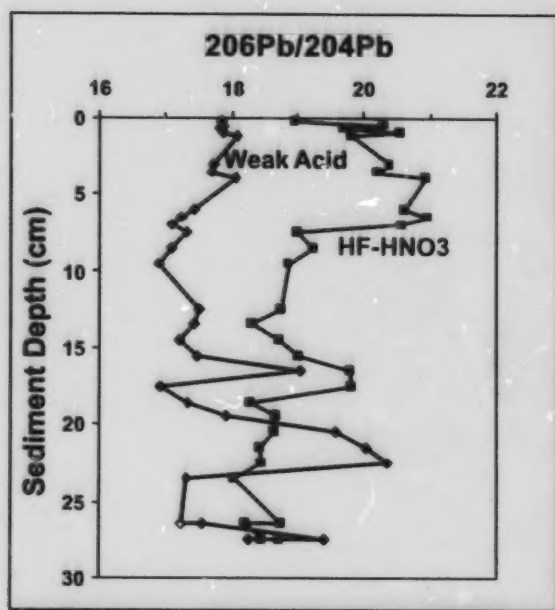


Figure 2-5

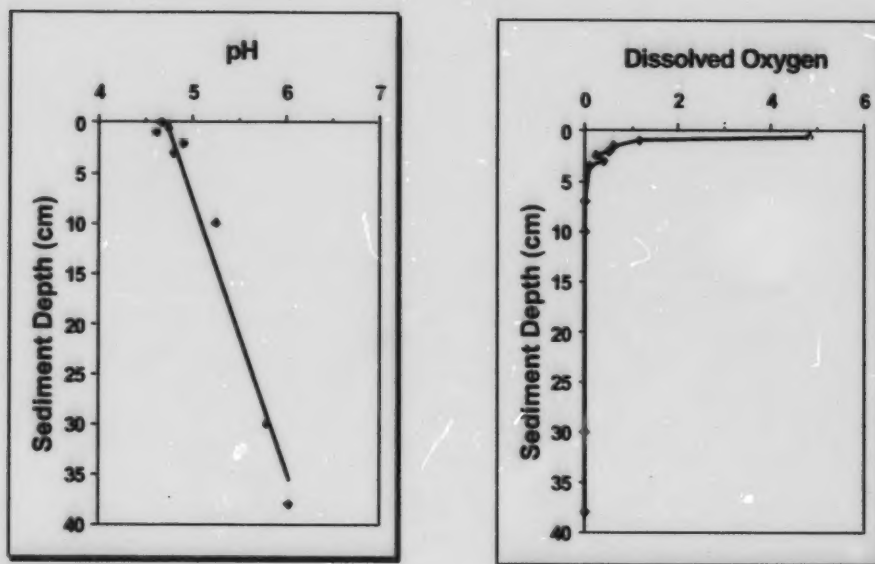
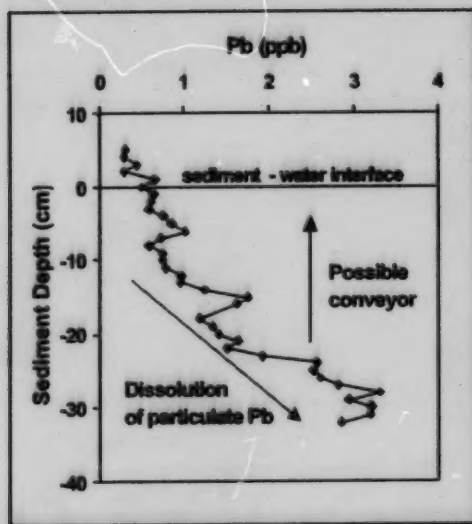


Figure 2-6



### 3. Atmosphere

#### 3.1 Solubilization of Gaseous Mercury by Sulfite

S. Scott

##### Objective

To investigate the solubilization of gaseous mercury by sulfite

##### Methods

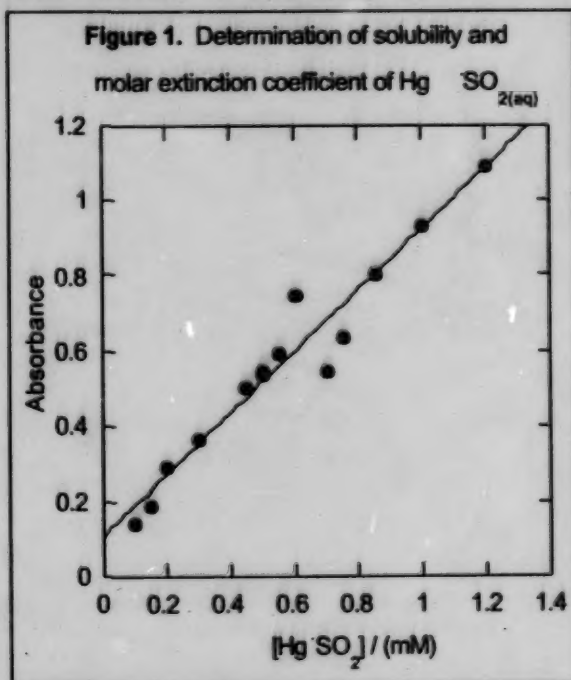
The best method we have thus far to prepare pure samples of the  $\text{Hg} \cdot \text{SO}_2(\text{aq})$  complex is the intramolecular redox reaction of  $\text{Hg}(\text{SO}_3)_2^{2-}$ , in the presence of a small excess of S(IV).

##### Results

Our unexpected discovery last year of the solubilizing effect of  $\text{SO}_2$  on  $\text{Hg}^0$  has major implications for the uptake of air-borne mercury by surface waters, and the retention of mercury in water bodies even after photoreduction. Therefore we have focussed our efforts this year on the characterization of the complex formed between  $\text{Hg}^0$  and  $\text{SO}_2$ , determination of its spectral properties and solubility, and investigation of its stability.

The best method we have thus far to prepare pure samples of the  $\text{HgSO}_{2(\text{aq})}$  complex is the intramolecular redox

reaction of  $\text{Hg}(\text{SO}_3)_2^{2-}$ , in the presence of a small excess of S(IV). (Conditions in which  $\text{Hg}^{2+}$  is in excess result in the well-known trapping of the  $\text{Hg}^0$  product of the redox reaction as  $\text{Hg}_2^{2+}$ .) In the former case, the final UV spectrum consists of a peak at 276 nm. When corrected for the (minor) contribution from  $\text{SO}_{2(\text{aq})}$  (since  $\text{HSO}_3^-$  does not absorb at this wavelength), the spectrum represents the complex  $\text{HgSO}_2$ . Its extinction coefficient was obtained by varying the initial concentration of  $\text{Hg}(\text{SO}_3)_2^{2-}$ , and measuring the final absorbance. The relationship is linear, Figure 1. Strict adherence to Beer's law, with  $\epsilon = (163 \pm 12) \text{ M}^{-1} \text{ cm}^{-1}$ , indicates that the equilibrium constant

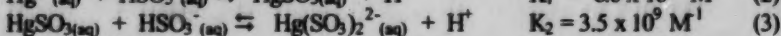
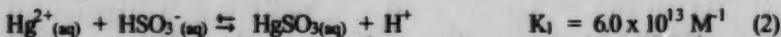


for formation of the complex is large, eq (1), and the product is completely soluble in water up to the mM level.



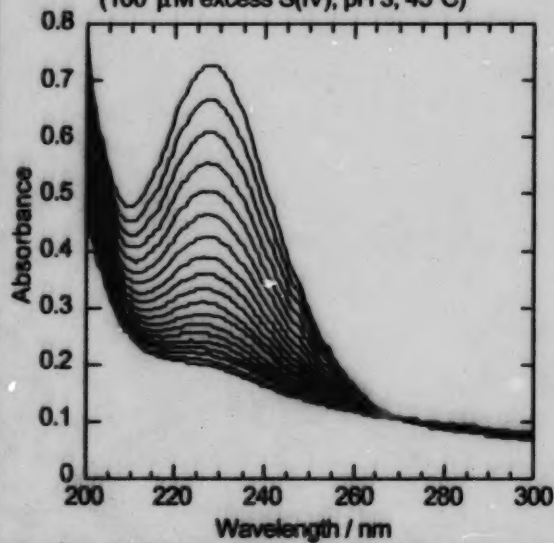
The latter finding is especially significant since it indicates that the presence of very small levels of  $\text{SO}_2$  can increase the solubility of  $\text{Hg}^0$  in water by *at least four orders of magnitude*. Studies to date have universally assumed the solubility of  $\text{Hg}^0$  in environmental waters to be the same as in distilled water, which is obviously and dramatically erroneous. It is not yet known at this time whether highly soluble  $\text{SO}_2$  forms a complex with dissolved  $\text{Hg}^0$ , or whether atmospheric (gaseous)  $\text{SO}_2$  carries  $\text{Hg}^0$  into the aqueous phase as the soluble  $\text{HgSO}_2$  complex.

Our earlier investigations, in the context of this project, of the binding of aqueous sulfite to  $\text{Hg(II)}$  resulted in the identification, spectroscopic characterization and stability of two complexes,  $\text{HgSO}_3$  and  $\text{Hg}(\text{SO}_3)_2^{2-}$ , eq (2-3).



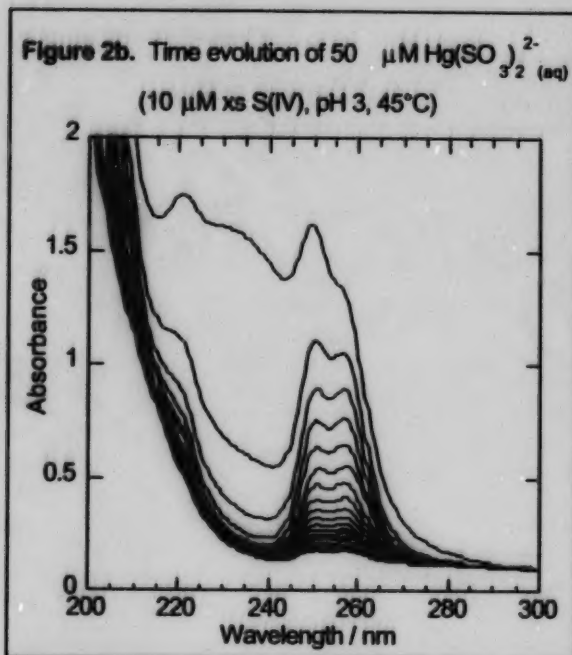
The measurement of these sequential binding constants was crucial to the evaluation of the speciation of the mercuric ion in waters containing  $\text{S(IV)}$ , and demonstrated that all

**Figure 2a.** Time evolution of 40  $\mu\text{M}$   $\text{Hg}(\text{SO}_3)_2^{2-}_{(\text{aq})}$   
(100  $\mu\text{M}$  excess  $\text{S(IV)}$ , pH 3, 45°C)



note is the appearance of a clean isosbestic point at 270 nm, which is typical of a reaction with no long-lived intermediates.

mercuric ion in atmospheric water should exist in one of these two forms. Although hydrogen sulfite is more abundant than  $\text{Hg}^{2+}$  under all environmentally-relevant conditions, reduction to  $\text{Hg}^0$  takes place only via the intermediacy of unstable  $\text{HgSO}_3$ . We have also reported quantitative measurements of the rate of this process, which is inhibited by sulfite, under conditions where the major mercury species is  $\text{Hg}(\text{SO}_3)_2^{2-}$ . This complex exhibits a peak in the UV at 230 nm which slowly decays in a pseudo-first-order process as sulfite dissociates and the  $\text{HgSO}_3$  thus formed decomposes to  $\text{Hg}^0$ , Figure 2a. Of special



In the course of our investigation of  $\text{HgSO}_2$ , which necessitated the use of lower sulfite concentrations, we observed dramatic and unexpected changes in the spectral profile, Figure 2b. Specifically, new peaks appear at 221, 249 and 254 nm, upon mixing  $\text{Hg}^{2+}$  with  $\text{HSO}_3^-$ . These peaks correspond neither to the known  $\text{Hg}(\text{SO}_3)_2^{2-}$  nor the unstable  $\text{HgSO}_3$  whose spectrum we recently reported for the first time ( $\lambda_{\text{max}} 232 \text{ nm}$ ). It is notable that *no other mercury-sulfite complexes have been observed or proposed* in any previous investigation. Yet we find clear evidence that additional, strongly absorbing mercury complexes are formed in a specific low concentration

regime. The appearance of these complexes also perturbs the kinetic behavior of the system, resulting in a pronounced wavelength-dependence of the observed rate constant,

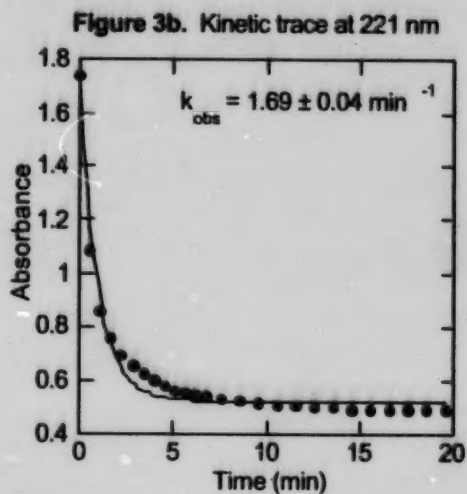
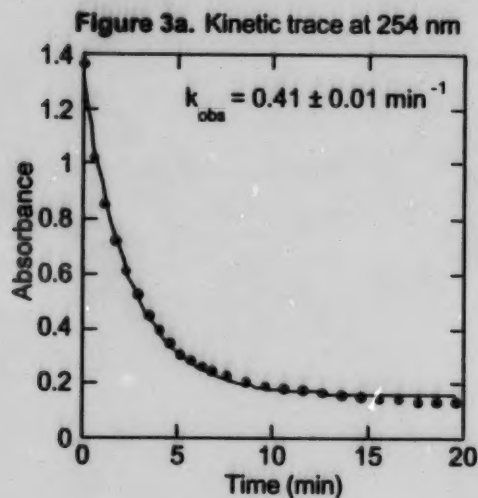


Figure 3.

Furthermore, while the behavior at 254 nm is pseudo-first-order, as shown by the exponential fit in Figure 3a, the fit is clearly inadequate at 221 nm (Figure 3b) and is suggestive of a biphasic profile. Thus a kinetically significant intermediate is formed under these conditions. While its identity is still unknown, its importance in defining the dynamics of the mercury-sulfite system at low concentrations will make it the focus of our work in the remaining months of the project.

## 4. Hg-Flux

### 4.1 Water- Air and Soil-Air Fluxes of Mercury

*S. Beauchamp*

#### Objectives

- To calibrate measurement systems and validate methodologies used in mercury flux measurements
- To quantify direct atmospheric input of total and methyl mercury through wet deposition processes (precipitation)
- To quantify air-surface mercury (gas) exchange in selected terrestrial and aquatic landscapes.
- To assess selected physical (meteorological) and chemical (substrate Hg concentration) factors regulating air-surface mercury exchange.
- To provide input to atmospheric and ecosystem based mercury cycling models.

#### Methods

- Calibrations, methodology checks and other QA/QC procedures were completed. Instrument performance was consistent, reliable and, where feasible, traceable. Flux chamber blanks were consistently low (near zero in many cases) while mercury injection and recovery tests showed chamber recoveries were 95-100%. Twenty-four flux measurements have been made at 16 locations (8 soil, 6 freshwater, 1 marine and 1 vegetation) under varying environmental conditions. Methodology checks showed that flux measured over water was not sensitive to variable flow rate through the chamber. Flux over soil was highly variable however this variability was traced to variations in soil moisture and not specifically to flow.
- Mercury air-surface exchange (flux) measurements over soil have been conducted at 8 forested sites and one open field site in Kejimikujik National Park comprising representative landscapes and substrate geochemistry. Additional experiments were conducted to measure mercury flux from a white pine tree. Flux measurements from vegetation were repeated again in 2001 under more favorable conditions in order to assess potential Hg flux per unit leaf area from white pine trees and the importance of meteorology (temperature/sunlight) in mediating this process (Figure 4.1).
- Mercury air-water gas exchange measurements were made at 9 freshwater sites including clear vs. colored lakes and a bog drainage stream contrasting in organic content and bedrock / surficial geology.
- Mercury flux measurements were accompanied by supporting measurements or air/soil temp, relative humidity, solar radiation, winds speed / direction and soil moisture measurements.

- Measurements of mercury flux using the dynamic flux chamber method continued in the third year of this study with measurements repeated at 2 aquatic sites that differ in water chemistry and organic content. These mercury flux measurements were conducted in conjunction with intensive diurnal measurements of aquatic Hg transformation made by O'Driscoll and Siciliano of selected mercury species (e.g. methyl vs. dissolved elemental mercury) in order to gain insight into biotic and abiotic factors regulating mercury methylation and de-methylation with respect to water chemistry and microbial activity. Mercury flux data and analysis is completed and water sample analysis is in progress. Integrated results and analyses are pending.
- Over the past two years continuing into the current fiscal year selected physical/chemical measurements were made in conjunction with each flux measurement. Meteorological measurements included air temperature, soil (water) temperature, relative humidity, soil moisture, incoming solar radiation, wind speed and direction. In addition, substrate samples (soil or water) were collected after each measurement for analysis of total mercury content in that substrate.
- Meteorological measurements have been analyzed along with mercury flux using multivariate statistical procedures (factor analysis) to determine the relative importance of these factors in regulating mercury flux. Using data sets pooled by substrate type (soil or water) mercury flux over all substrate types were closely associated with solar radiation but not temperature (soil or water) as might be expected from simple Henry's Law dynamics.
- Spectral measurements of chamber materials confirmed that Teflon allows wavelengths of solar radiation through to the measurement surface. Additional experiments showed that flux was not sensitive to UV-B but was very responsive to thermal change (see Lean et al 2000).
- Total mercury concentration and wet deposition is continuing under a separate program but methyl mercury was added in June 2001 under TSRI to compliment TSRI related in-lake and soil related processes research and modeling studies. Methyl mercury samples are currently being analyzed and results are pending.
- Gaseous elemental mercury, total and methyl mercury in precipitation data collected, in part under TSRI 124/105 has been used for US and Canadian atmospheric model input and evaluation.
- The relationship between mercury flux, substrate composition and other physical (meteorological) variables (Figure 4-4) is being incorporated into an ecosystem-based model to assess sources and environmental cycling pathways of mercury within ecosystems and subsequently into biota.

## Results

- Results of individual flux measurements are summarized in Table 4-1. In each case substrate type, geochemistry and environmental variables have been measured and multivariate statistical analysis completed.
- Mean diurnal mercury flux rates measured over undisturbed soils were generally low (1.2 ng/m<sup>2</sup>/hr, n=8) and similar to mean flux rates over clear and colored water (1.3 ng/m<sup>2</sup>/hr, n=10).
- White pine (Figure 1) tree showed a large range in mercury flux ranging from -17 to +29 ng/m<sup>2</sup>/hr. Results of measurements of mercury flux from a white pine tree flux suggest that vegetation may play an important role in the air-surface exchange of mercury.
- Preliminary analyses of flux data suggest that evasion, the net release of mercury from the surface to the atmosphere, is the dominant process over a diurnal cycle. Deposition of gaseous mercury to the surface was generally measured at night.
- When sites are analysed individually, relationships between temperature and flux become more apparent (Figure 4-2).
- Laboratory experiments under constant light regimes indicated that soil moisture might also influence flux rates with highest flux measured over near saturated soil. Flux rates progressively diminished as soils were allowed to dry with little or no flux occurring over dry soil.
- Mercury flux rates over soil and water surfaces were not statistically correlated ( $p < 0.05$ ) with total mercury content in the substrate (Figure 4-3). Mercury flux in freshwater lakes was not significantly different in clear vs colored lakes. This indicates that although some abiotic factors may be important in mercury reduction and gas exchange, there are other mitigating factors (eg organic ligands, biotic factors), which also drive the mercury cycle in soil and water.

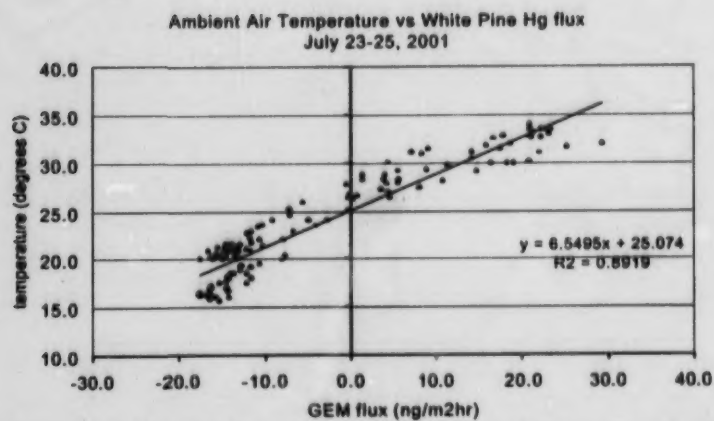
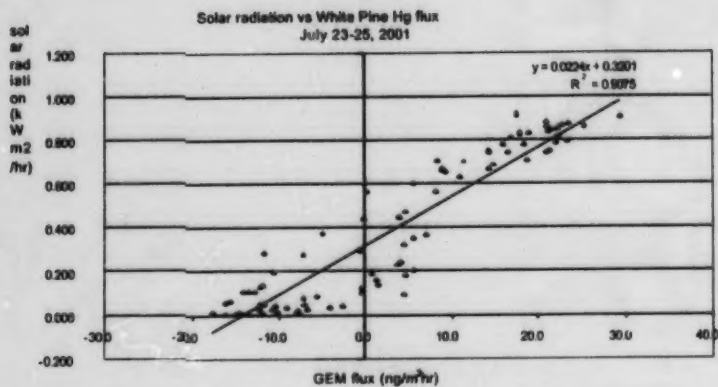


**Figure 4-1:** Relationship between mercury flux from a white pine tree and solar radiation (top) and temperature (bottom).

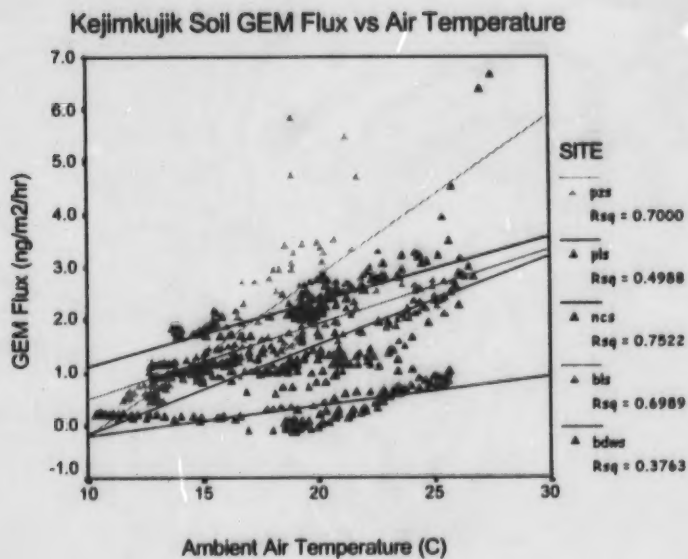


**Figure 4-2:** Individual site variability in the relationship between temperature and soil mercury flux.

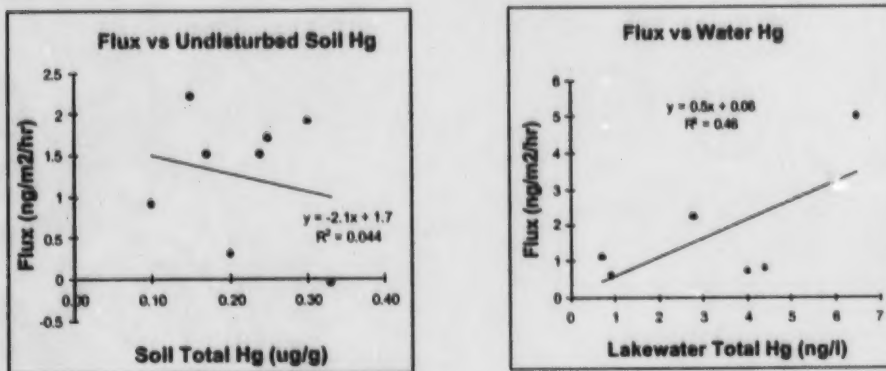


**Figure 4-3:** Mercury flux from soil and water surfaces versus total mercury content in the substrate. Linear relationship is not statistically significant in either case ( $p > 0.05$ ).

**Table 4-1.** Mercury flux measurement sites, substrate and substrate type, substrate total mercury concentration, mean daily (24 hr) mercury flux rate, daily range in mercury flux and chamber blank flux.

| Substrate Type       | Site (year) | Substrate Type | Substrate Total Hg.<br>Hg <sub>tot</sub> µg/g | 24 hr mean Hg Flux<br>ng/m <sup>2</sup> /hr | Hg Flux Range<br>ng/m <sup>2</sup> /hr | Blank Flux<br>ng/m <sup>2</sup> /hr |
|----------------------|-------------|----------------|-----------------------------------------------|---------------------------------------------|----------------------------------------|-------------------------------------|
| <b>NATURAL SOIL</b>  |             |                |                                               |                                             |                                        |                                     |
|                      | BDW - 1997  | forest soil    | 0.33                                          | -0.4                                        | -1.3 to 1.0                            | n/a                                 |
|                      | BDW - 1999  | forest soil    | 0.20                                          | 0.3                                         | -0.2 to 1.5                            | 0.24                                |
|                      | PUZ - 1999  | forest soil    | 0.24                                          | 1.5                                         | 0.5 to 5.7                             | 0.18                                |
|                      | NCL - 1997  | forest soil    | 0.30                                          | 1.9                                         | 1.1 to 3.3                             | n/a                                 |
|                      | NCL - 1999  | forest soil    | 0.15                                          | 2.2                                         | 1.8 to 3.0                             | 0.05                                |
|                      | CAP - 1997  | glacial till   | 0.10                                          | 0.9                                         | -0.7 to 3.8                            | n/a                                 |
|                      | PL - 2000   | granite/till   | 0.17                                          | 1.5                                         | 0.6 to 4.0                             | 0.06                                |
|                      | BL - 2000   | granite/till   | 0.25                                          | 1.7                                         | 0.9 to 3.1                             | 0.08                                |
| <b>IMPACTED SOIL</b> |             |                |                                               |                                             |                                        |                                     |
|                      | CAP - 1999  | disturbed      | 0.14                                          | 8.0                                         | 5.1 to 20                              | 0.14                                |
|                      | CAP - 2001  | disturbed      |                                               | 28.7                                        | 12.1 to 68.                            | 0.0                                 |
|                      | CAR - 1998  | mine tailing   | 2.15                                          | 130.                                        | 53. to 415.                            | 5.0                                 |
|                      | GOL - 1998  | mine tailing   | 2.13                                          | 237.                                        | 116. to 640.                           | 15.4                                |
| <b>FRESH WATER</b>   |             |                |                                               |                                             |                                        |                                     |
|                      | BDW - 1997  | high DOC       | 6.5                                           | 5.0                                         | 0.5 to 44                              | 0.05                                |
|                      | BDW - 2000  | high DOC       | 4.0                                           | 0.7                                         | 0.0 to 2.3                             | 0.39                                |
|                      | BDW - 2001  | high DOC       | 5.6                                           | 1.1                                         | -0.2 to 6.5                            | 0.07                                |
|                      | PUZ - 1999  | low DOC        | 0.9                                           | 0.6                                         | -0.1 to 2.5                            | 0.10                                |
|                      | PUZ - 2001  | low DOC        | 1.9                                           | 0.9                                         | -4.5 to 16.                            | 0.07                                |
|                      | NCL - 1997  | med DOC        | 2.8                                           | 2.2                                         | -0.3 to 13.                            | 0.03                                |
|                      | PL - 2000   | high DOC       | 4.4                                           | 0.8                                         | 0.1 to 2.2                             | 0.18                                |
|                      | BL - 2000   | low DOC        | 0.7                                           | 1.1                                         | 0.3 to 3.0                             | 0.08                                |
|                      | TMB - 2000  | high DOC       | 5.4                                           | 0.0                                         | -0.3 to 0.4                            | 0.10                                |
| <b>MARINE</b>        |             |                |                                               |                                             |                                        |                                     |
|                      | HFH - 1999  | salt water     | 0.8                                           | 0.7                                         | 0.1 to 2.3                             | n/a                                 |
| <b>VEGETATION</b>    |             |                |                                               |                                             |                                        |                                     |
|                      | Pine - 2000 | 2m tree        | n/a                                           | 0.4                                         | -2.1 to 8.3                            | 0.0                                 |
|                      | Pine - 2001 | 2m tree        | n/a                                           | -3.6                                        | -17.7 to 29.                           | 0.11                                |

Note: 1997 data from Boudala *et al.* (1999), BDW = Big Dam West Lake, PUZ = Puzzle Lake, NCL = North Cranberry Lake, CAP = CAPMoN air chemistry site, BL = Beaverskin Lake, PL = Pebbleloggitch Lake, TMB = Thomas Meadow Brook (bog drainage), CAR = Caribou Mine tailings, GOL = Goldenville Mine tailings, a = gold mine sites used mercury amalgamation process. Mine tailing soil mercury data from Wong *et al.* 1999, HFH = Halifax Harbour, Pine = 2m White Pine Tree, n/a = not available.

## 5. Water

### 5.1 Mercury Speciation and Microbial Transformations

*D.R.S. Lean, S. Siciliano, J. Holmes, and N.J. O'Driscoll*

#### Objective

- To identify processes leading to MeHg inputs to the lakes in Kejimikujik
- To develop simple microbial assays to test for mercury transformations in the ecosystem.

#### Methods

- Methyl mercury analysis was performed by clean sampling techniques, extraction onto sulphhydryl cotton and pre-concentration in DCM before analysis by GC-AFS.
- Results indicated wetland inflow and groundwater as potentially high sources of MeHg to lakes
- Mercuric reductase and peroxidase assays have been developed to estimate the reduction of inorganic mercury to elemental and the oxidation of elemental mercury to inorganic.

#### Results:

Table 5-1

| Samples | MeHg<br>pg/L | Samples | MeHg<br>pg/L | Samples | MeHg<br>pg/L |
|---------|--------------|---------|--------------|---------|--------------|
| 28      |              | 81      |              | 156     |              |
| 37      |              | 88      |              | 255     |              |
| 38      |              | 88      |              | 434     |              |
| 41      |              | 98      |              | 1109    |              |
| 60      |              | 101     |              | 1179    |              |
| 61      |              | 103     |              | 2031    |              |
| 70      |              | 105     |              | 2323    |              |
| 74      |              | 146     |              | 3779    |              |
| 79      |              |         |              |         |              |

- The results from the microbial assays indicate that microbial transformations significantly affect levels of DGM in lake water. The microbial assays also provided a good rationale for the diurnal fluctuations in DGM. Increasing mercuric reductase activities corresponding to increases in DGM in the morning and increasing peroxidase activity corresponding to the decrease in DGM during the afternoon. Our results indicate that microbial transformations play an important role controlling the fate of DGM in lake water.

## 5.2 Continuous Analysis of Dissolved Gaseous Mercury

*N.J. O'Driscoll and D.R.S. Lean*

### Objective

- To develop a method for the near continuous analysis of dissolved gaseous mercury (DGM) in remote freshwater locations.
- To use DGM variations in diurnal cycles to develop a predictive model based on water chemistry
- To relate DGM and water chemistry variations to mercury flux and meteorological measurements

### Methods

- A Tekran 2537A automated mercury analyzer was modified with a 1L glass sparger that received a continuous flow of lake water. The water was sparged using air supplied by a Tekran 1100 zero air generator. A Hydrolab was used in-line so that DGM and water chemistry measurements could be made every 5 minutes (Submitted for publication to Sci. Tot. Env.).

### Results:

- Method testing indicated that the continuous method produced results that are comparable with the discrete analysis method (most commonly used). 600 readings of DGM can be taken over a 48-hour period using the method developed as compared with 48 using the discrete method.
- Results from 48 hours sampling periods were performed on Big Dam West and Puzzle Lake in Kejimikujik Park, Nova Scotia. The DGM and pH results for Puzzle are shown Figures 5-1 and 5-2 respectively.
- Results are being integrated with Flux and meteorological measurements from Steve Beauchamp
- A predictive model for DGM and Hg volatilization is being developed based on this work.

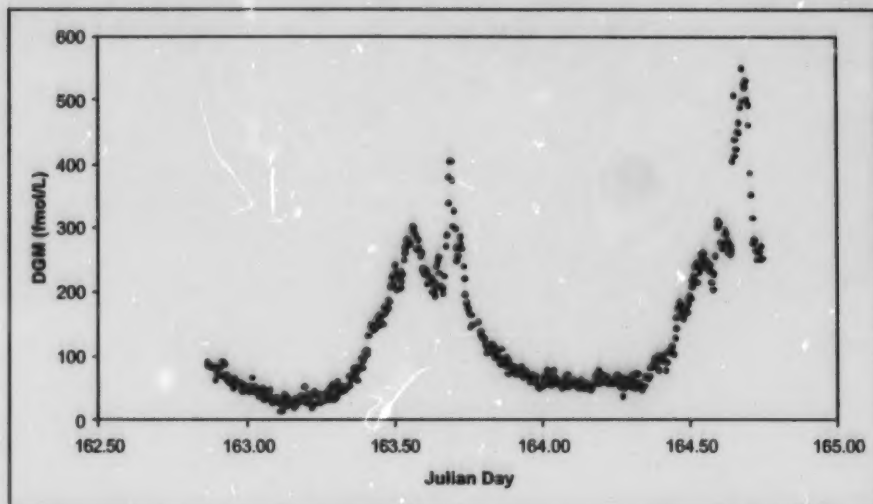


Figure 5-1: DGM in Puzzle Lake over 48 hour time period

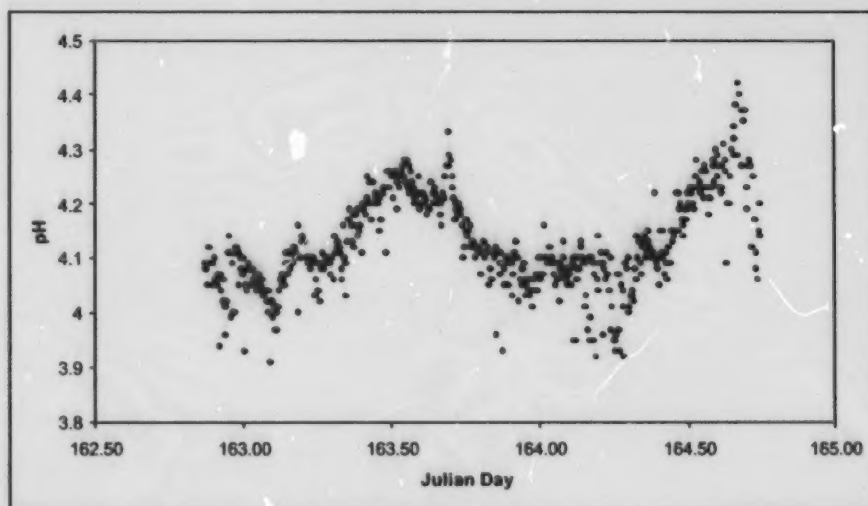


Figure 5-2: pH in Puzzle Lake over 48 hour time period

### 5.3 Relations of Mercury and Water Chemistry to Geology

*A.L. Sangster, P.K. Smith, and G. Hall*

#### Objectives

- Additions of mercury to the atmosphere over geologic time originate from bedrock sources. These additions are made in various ways, for example, the burning of fossil fuels, the smelting of Hg-bearing ores, volcanic eruptions, and slow evolution of Hg from bedrock during processes of oxidation and erosion. Once in the atmosphere, mercury cycles to the earth's surface where it is incorporated in biological and abiotic processes. A portion is fixed, largely in organic media, and a portion eventually returns to the atmosphere. At the earth's surface, differentiation between recycled Hg returning to the atmosphere and primary Hg evolving from bedrock is difficult. The largest portion of geogenic Hg contributed to the atmosphere is through major tectonically active zones that girdle the earth (Kesler, 1994, Schlüter, 2000). In a historical context, the sedimentary rocks of the Meguma Group that underlie southwestern Nova Scotia were part of the abyssal plain marginal to the proto-Taconic Orogen that formed 600 to 480 million years ago. Rocks of the Halifax formation were time equivalents of the early volcanism in the orogen. They are rich in organically derived carbon (up to 2 %  $C_{org}$  = 6 to 8 % fresh organic material) and would have constituted a suitable sink for the entrapment of Hg in the rocks.
- The original proposal for this project addressed two objectives for the water sampling. First, to determine whether or not there might be a concentrated bedrock source of mercury within the park area, and secondly, if such a source could be found, and if it contained anomalous high  $SO_4$ , to investigate the isotopic composition of the aqueous sulphate to see whether the isotopic signature could be related to a bedrock rather than an atmospheric source. The associated bedrock sampling program not reported on here is investigating the Hg variations within the various bedrock lithologies in the park area.
- The regional water sampling is designed to investigate the potential for mercury additions to the environment either from a concentrated source in bedrock or from possible elevated backgrounds in some bedrock lithologies.
- To date approximately 250 water samples have been collected and analysed during 4 periods of sampling in the field; August and November, 1999, and June and August, 2000. All sizes of drainage have been sampled

#### Methods

- Water sampling was carried out in and south of Kejimikujik Park to give a representative sample distribution over various bedrock lithologies present. All sizes and drainage types were sampled with an emphasis on sampling headwater streams and bogs which may show elevated bedrock signatures if present.

- Sampling and analysis for mercury, anion and cation analyses was carried out following procedures developed in the Geological Survey of Canada (Hall, 1996, Hall et al., 1998). Materials used for sample collection; 50 ml syringe (Delta Scientific 6602-2016), and Millipore Sterivex-HV 0.45  $\mu$ m cartridge filter (Millipore SV-HU010RS). Samples were collected in 60 ml nalgene HDPE wide mouth bottles (Fischer 03-313-4B)
- Samples for Hg, anion, and cation analyses were collected as follows. At the sample site, the syringe was first vigorously rinsed twice with the stream water to be sampled. The syringe was then filled and fitted with a cartridge filter and water was extruded through the filter into pre-numbered 60 ml sample bottles. Each of three sample bottles was vigorously rinsed with filtered water from the sample site. Normally, a little more than 3 syringes were required to fill 3 sample bottles at each site. While in the field, samples were kept cool in a lunch box cooler containing ice packs. Daily, upon returning to base from the field, the cation sample was acidified with 0.5 ml of 1% ultra-pure nitric acid and 1 ml of EPA standard bromine chloride was added as a preservative to the sample for mercury analysis. Samples were refrigerated in the field base and shipped in refrigerated coolers to the laboratories of the Geological Survey of Canada where they remained refrigerated until analysis. Standards were added to the sample population in the field by sampling de-ionized water following the procedure outlined above.
- Hg analyses were carried out in on a Tekran Hg analyser, and cation and anion analyses were carried out by ICP MS/ES and ion chromatography respectively, in the laboratories of the Geological Survey of Canada.

## Results

A number of observations based on a preliminary review of the data are itemized below.

- Ranges in values of Hg in waters are from the detection limit of 0.5 ppt to a maximum of 27.7 ppt in the samples analysed to date. DOC values in the same samples range from 1 ppm to 91 ppm. There is a strong positive correlation between Hg and DOC (Figure 5-3). The highest Hg value of 27.7 ppt comes from drainage at the Whiteburn Gold District and may be from contamination from gold processing in the 1800's.
- The pH values of waters in the area sampled vary from 3.5 to 7 with a maximum between 4 and 5.25 (Figure 5-4).
- The maximum DOC and Hg values at a given pH decrease as pH increases (Figure 5-5), probably reflecting the decreased Hg carrying capacity as DOC is oxidized in the surface environment.
- The analyses of both Hg and DOC show a near lognormal frequency distribution (Figure 5-6) suggesting that the samples represent a single population without

significant anomalous samples. Irregularities in the distributions, most obvious in the log-normal plots, probably reflect varying compositions from samples collected in different sampling periods with different water levels.

- The limited number of sulphate analyses available does not seem to indicate a significant bedrock source of sulphate. The samples awaiting analysis contain a larger number of samples collected over sulphide-rich areas of bedrock.
- In spite of the lack of evidence for a bedrock Hg source in the data presented here, a preponderance of the samples with higher DOC and Hg values occur over the black sulphidic slates of the Halifax Formation (Maps 1, Map 2). Areas of note include the slates near the Goldenville-Halifax formation contact south-east of the park, the area south and south-east of Kejimikujik Park, and the area north of the Mersey River in the north eastern part of the park. Some higher values occur over the Kejimikujik granite along the Luxton Lake trail north of Lucifer Brook. Some or all of the values southeast of Kejimikujik Lake may be related to the interpreted presence of the Liscombe Fault.
- It is suggested that this control on the Hg and DOC anomalism results from favourable conditions for bog formation over the black slates. The slate terrain is flatter, in part poorly drained, tends to have more clay-rich till, and contains a high bedrock sulphide content that may reduce the viability of more luxuriant forms of vegetation. It is also suggested that the high sulphide content of bedrock, and possibly higher trace metal contents than those of other lithologies, may have a nutrient effect on bog biota.

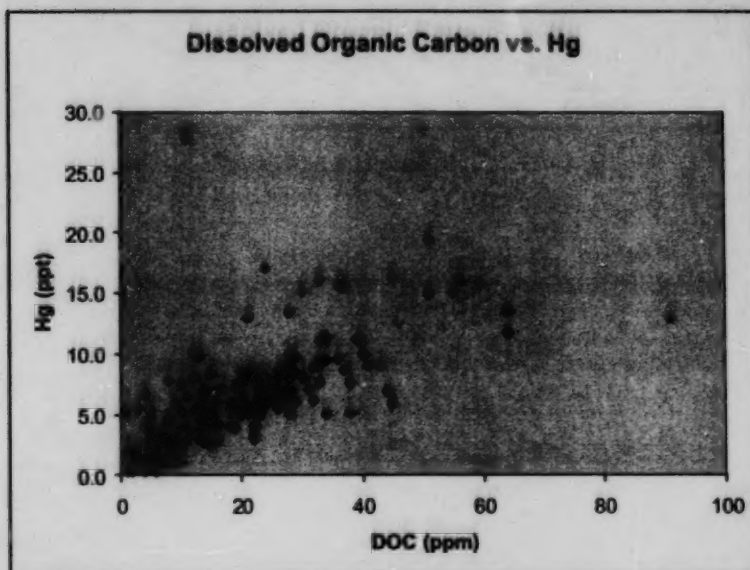


**Figure 5-3:** Hg shows a strong positive correlation with DOC in all waters analysed to date. The samples in this diagram represent 204 samples collected in four sampling periods over 2 years including samples from lakes, streams, bogs, springs and a few wells.

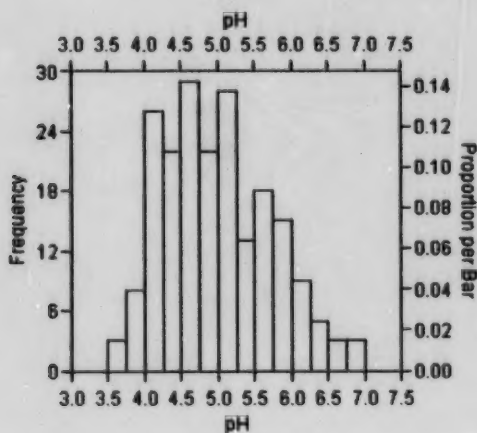


**Figure 5-4:** The distribution of pH values is from a low of 3.5 to a high of 7. About 60 per cent of the values are between 4 and 5.25.

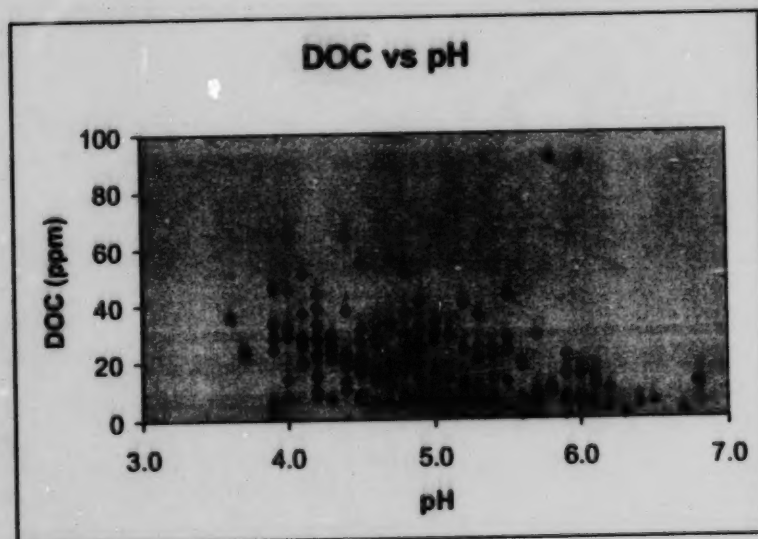
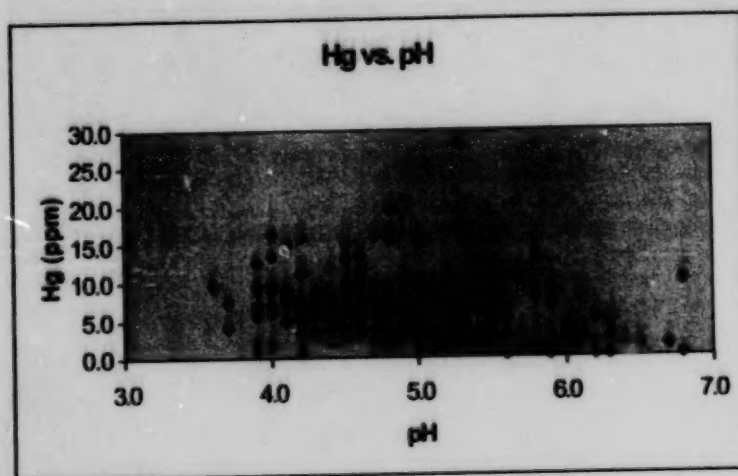


**Figure 5-5:** Both DOC and Hg values in surface water decrease with rising pH. This is most likely a result of the oxidation of DOC by sunlight as water travels down drainage.

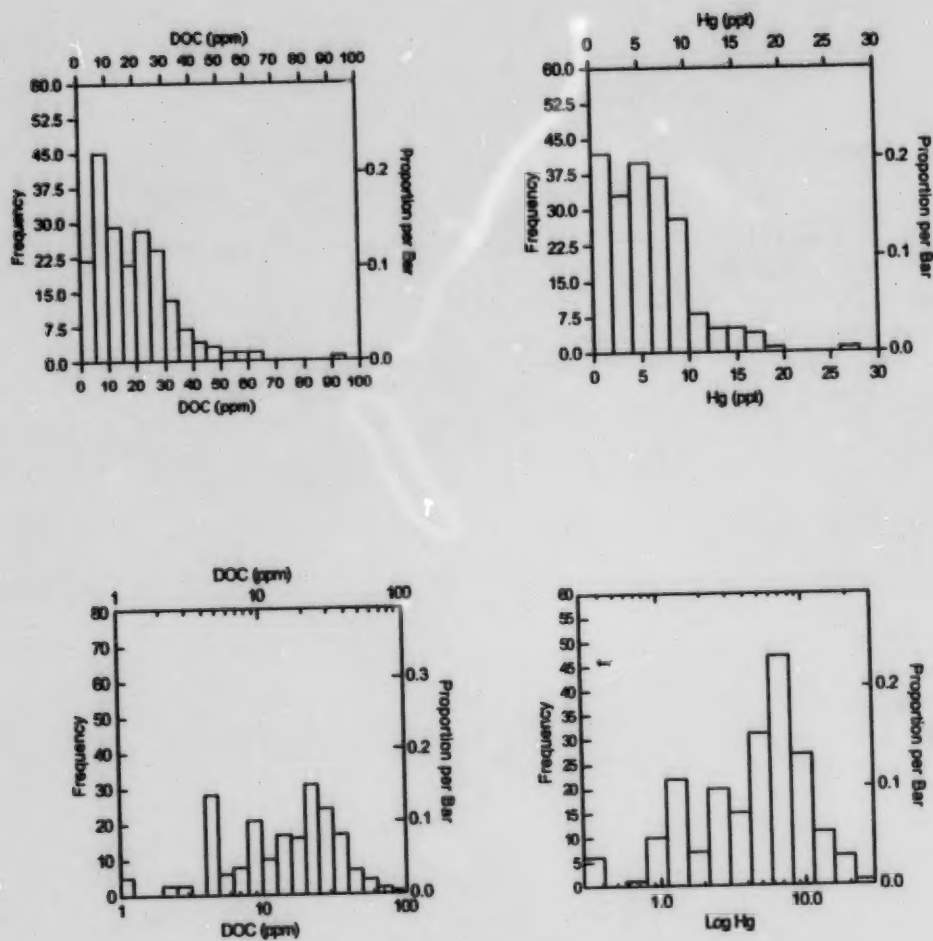


**Figure 5-6:** Normal and log frequency distribution histograms for DOC and Hg in waters indicate that the values approximate a simple spectrum of values with little evidence of an anomalous population. The irregularities in the logarithmic distribution may reflect differences in the populations collected at different seasons and at different water levels.

## 5.4 Groundwater Mercury Inputs to Big Dam West Lake

A. Rencz, T. Peron and M. Robin

### Objective

- To quantify the amounts of total and methyl mercury inputs into BDW from groundwater
- To identify the importance of groundwater in contributing to total and methyl mercury mass budgets in Kejimikujik Park

### Methods

- In order to get samples of groundwater and to quantify the amount of groundwater flowing into Big Dam West Lake, a series of mini-piezometers and seepage meters were installed at various locations within the lake. Sites were chosen based on the physical properties (appearance) of the lake bottom and depth of the water column. Areas with minimal boulders, and where the lake bottom appeared to be mostly sandy containing only pebble and cobble size rocks, were preferred installation sites. The water depth at these sites was generally between one and three feet deep.
- Installed 11 lake bottom piezometers and 4 seepage meters in BDW
- Sampled piezometers intermittently from June until mid-September
- Sampled well waters at several locations.
- Analysis for methyl mercury (MeHg), total Hg, dissolved organic carbon (DOC) and cations.

### Results

- Eleven of thirteen mini-piezometers installed, were successful in producing groundwater. In the month of June the rate of groundwater inflow to the lake was highest at a rate of approximately 4.26 mL/min and coincidentally the results for total Hg were highest during this initial sampling session.
- Total Hg in groundwater ranged between 0.7 and 6.5 ppt, with a mean of 2.98 ppt for the month of June.
- Sampling in July was more successful due to more efficient sampling equipment and more mini-piezometers being installed at Big Dam West Lake. Average Groundwater input to the lake was calculated to be 1.83 mL/min, and the Average Hg input was 0.825 ppt. Total Hg values ranged between 0.3 and 3.0 ppt for the month of July.

- Flow rates from piezometers for June to September only. These were extrapolated to the rest of the year (assumed May flow would be similar and October was used to provide average values for November to April)
- Preliminary calculations indicate that 52 g. of Hg is input into BDW each year
- Results received thus far indicate that over half the samples analyzed have total mercury values less than or equal to 0.75 ppt. August and September were very successful sampling sessions, however the total Hg results are not yet available from the lab. A significant number of samples for Methyl Mercury determination were also acquired from the mini-piezometers, although the results are not yet available.

Table 5-2

**Case Summaries**  
**HG\_PPT**

| MONTH | N  | Mean  | Median | Std. Error of Mean | Minimum | Maximum | Std. Deviation |
|-------|----|-------|--------|--------------------|---------|---------|----------------|
| JUN   | 7  | 2.986 | 2.700  | .796               | .7      | 6.5     | 2.106          |
| JUL   | 18 | .825  | .615   | .164               | .3      | 3.0     | .697           |
| Total | 25 | 1.430 | .720   | .312               | .3      | 6.5     | 1.560          |

Table 5-3: Seepage Meters

| Seep 1                              | Flow Rate | Seep 2        | Flow Rate | Seep 3        | Flow Rate | Seep 4        | Flow Rate  | Monthly Average |
|-------------------------------------|-----------|---------------|-----------|---------------|-----------|---------------|------------|-----------------|
| 6/9/01 9:04                         | 7.0000    | 6/9/01 10:20  | 2.2826    |               |           |               |            |                 |
| 6/9/01 14:34                        | 7.0000    | 6/9/01 14:56  | 2.2826    |               |           |               |            |                 |
| 6/9/01 14:45                        | 7.2414    | 6/9/01 14:58  | 7.4468    |               |           |               |            |                 |
| 6/9/01 19:35                        | 7.2414    | 6/9/01 19:40  | 7.4468    |               |           |               |            |                 |
| 6/10/01 13:20                       | 1.4399    | 6/10/01 13:42 | 0.1349    |               |           |               |            |                 |
| 6/11/01 9:18                        | 1.4399    | 6/11/01 9:28  | 0.1349    |               |           |               |            | 4.2576          |
| 7/10/01 13:00                       | 1.4185    | 7/10/01 13:00 | 0.1773    | 7/10/01 15:04 | 0.3493    |               |            |                 |
| 7/12/01 10:00                       | 1.4185    | 7/12/01 10:07 | 0.1773    | 7/12/01 13:50 | 0.3493    |               |            |                 |
| 7/12/01 10:05                       | 3.3014    | 7/12/01 10:15 | 7.5000    |               |           |               |            |                 |
| 7/12/01 14:57                       | 3.3014    | 7/12/01 14:55 | 7.5000    |               |           |               |            |                 |
| 7/12/01 15:00                       | 1.7531    | 7/12/01 15:00 | 4.2672    | 7/12/01 14:00 | 0.5161    |               |            |                 |
| 7/13/01 11:15                       | 1.7531    | 7/13/01 11:35 | 4.2672    | 7/13/01 13:15 | 0.5161    |               |            |                 |
| 7/13/01 11:15                       | 0.1717    | 7/13/01 11:50 | 0.2829    | 7/13/01 13:35 | 0.2827    |               |            |                 |
| 7/22/01 13:42                       | 0.1717    | 7/22/01 13:50 | 0.2829    | 7/22/01 15:45 | 0.2827    |               |            | 1.8200          |
| 8/15/01 17:00                       | 0.3883    | 8/16/01 16:00 | 0.3947    | 8/15/01 17:20 | 0.3623    | 8/15/01 17:50 | 0.30797101 |                 |
| 8/16/01 15:45                       | 0.3883    | 8/16/01 19:10 | 0.3947    | 8/16/01 16:20 | 0.3623    | 8/16/01 16:50 | 0.30797101 | 0.3633          |
| 9/13/01 13:00                       | 0.3704    | 9/13/01 13:10 | 0.3414    |               |           |               |            |                 |
| 9/15/01 10:00                       | 0.3704    | 9/15/01 10:05 | 0.3414    |               |           |               |            |                 |
| 9/15/01 10:00                       | 0.9091    |               |           |               |           |               |            |                 |
| 9/15/01 13:40                       | 0.9091    |               |           |               |           |               |            | 0.5403          |
| Average per Meter                   | 2.3994    |               | 2.5364    |               | 0.3776    |               | 0.3080     |                 |
| Seasonal Average (June - September) |           |               |           |               |           |               |            | 1.7453          |

## **6. Watersheds**

### **6.1 Hydrology, Mercury and DOC Modelling in Two Freshwater Lakes**

T. Clair, P. Arp, F.R. Meng, D. Lean, G. Brun

#### **Objectives**

- There were two main objectives to this study. The first was to produce a surface water input, output budget for two lakes, one with low dissolved organic carbon (DOC), and the other with high concentrations. The working hypothesis was that the higher DOC lake would have more Hg flushing through it than the low DOC one, as there is a strong, direct DOC:Hg correlation known to occur. We were also interested in knowing how much Hg was lost or generated in the lakes over a yearly cycle. This could be connected to other work to determine whether losses would be due to photochemical or sedimentological processes.
- The second study was to determine if we could determine Hg generation of catchments in the area, knowing catchment terrain characteristics. The working hypothesis was that the flatter the basin, the more wetlands would occur, the more DOC would be produced, and thus the greater would be Hg export.

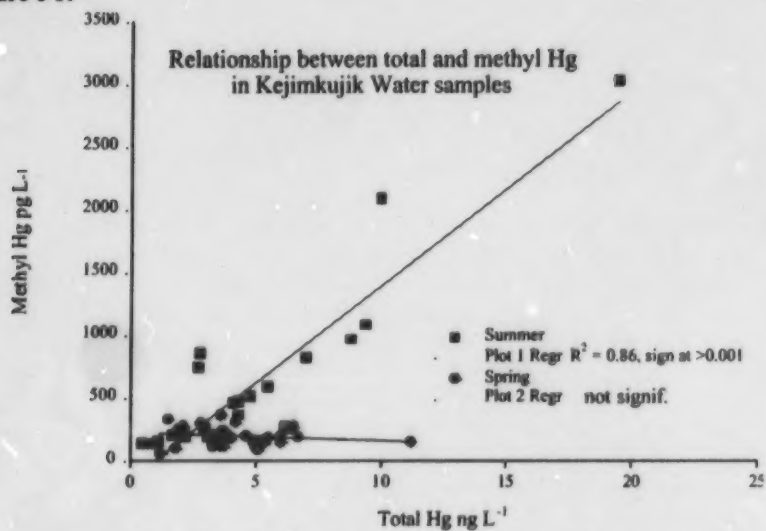
#### **Methods**

- For the lake budget study, we sampled input and output streams to Big Dam West (high DOC) and North Cranberry (low DOC) lakes. Monthly sampling has been done for four years, with methyl Hg being available for the last two years. The concentration data are being matched to runoff data generated by the ForHyMod hydrological model (Yanni *et al.* 2000) to produce monthly export estimates. The sampling program is ending November 2001, and preliminary budgets will be completed in the spring of 2002.
- In order to determine if basin characteristics controlled Hg exports, we sampled 26 streams in August 2000 and April 2001. We analyzed the catchments draining to the sampling sites using GIS methods. We therefore attempted to produce a statistical model which included general basin slope, slope at the sampling site, basin orientation as the main independent variables, to see if we could predict total and methyl Hg concentrations at the sites for both low flow (August), and high flow (April) conditions.

#### **Results**

- There is a very close statistical relationship between total mercury and methyl mercury in the Park waters in the summer, but not early spring the surface waters of Kejimikujik National. Methyl Hg is approximately 10% of the total (Fig. 6-1).

**Figure 6-1:**



- There is also a close relationship between dissolved organic carbon and total Hg in these basins in both summer and early spring (Fig.6-2). However, there is a relationship between methyl Hg and DOC only for the summer sampling and not the spring one (Fig. 6-3).

**Figure 6-2:**

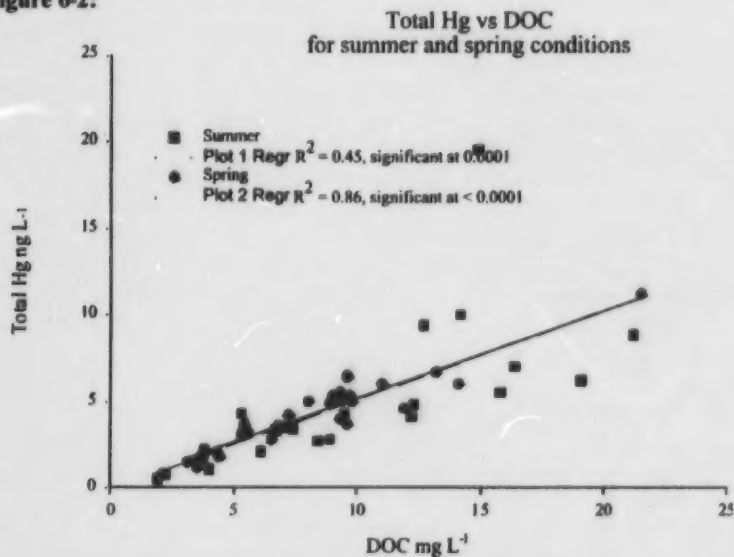
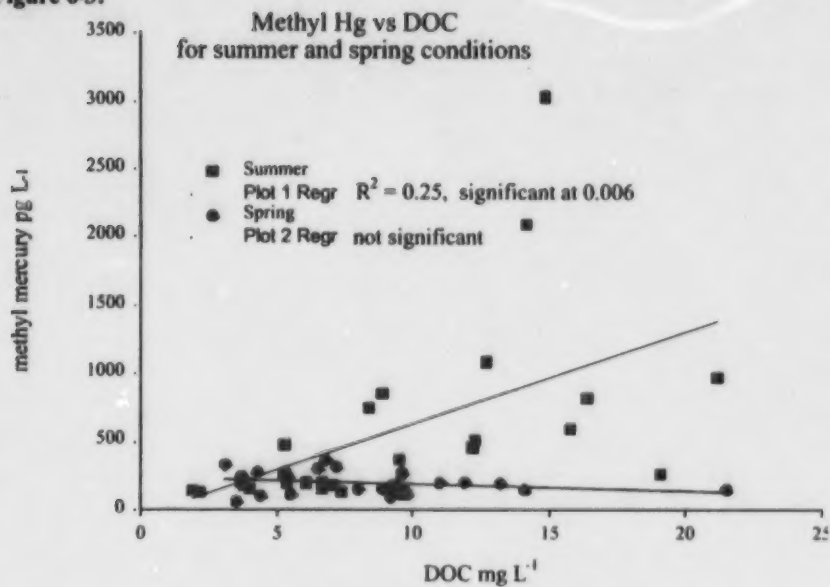


Figure 6-3:



- With the above information in hand, and with the use of GIS techniques, we have therefore been able to produce two statistical models that predict annual DOC and total Hg concentrations, as well as summer methyl Hg concentrations. A manuscript, which details the methods, is currently being prepared.

## 7. Geology

### 7.1 Mercury Content of Bedrock and Drill Core

*A. Sangster, P. Smith, and T. Goodwin*

#### Objectives

- In conjunction with the park bedrock sampling program, a program for the sampling of similar lithologies in drill core was carried out to evaluate the possible loss of Hg from bedrock as a result of surficial weathering.

#### Methods

- Surface samples of Halifax and Goldenville formations and the Kejimikujik Granite were collected from rock exposures in the Kejimikujik Park area. Subsurface samples of Halifax and Goldenville formations were collected from drill core stored in the Nova Scotia Department of natural Resources core storage facility in Stellarton, Nova Scotia. All weathered rinds and surficially exposed surfaces of the surface samples were removed with a diamond saw prior to analysis. Total Hg analyses were carried out by commercial laboratories and at the Geological Survey of Canada in Ottawa.
- Approximately 100 C horizon till samples were also collected during the 2000 and 2001 field seasons. 14 distinct rock types and a peat bog have been analysed for mercury content in, and adjacent to Kejimikujik Park (n=685).

#### Results

- Average Hg values are as follows:

Mixed Slate/Greywacke = 0.80ppb, Basalt = 0.97ppb, Greywacke = 1.1ppb, Hornfels = 1.2ppb, Granite = 1.5ppb, Siltstone = 1.63ppb, Black Slate = 1.89ppb, Gneiss = 2.83ppb, Quartz Veins = 6.40ppb, Grey-Green Slate = 7.61ppb, Shear Zone = 8.45ppb, Aplite = 9.50ppb, Biotite concentrates = 13.77ppb, Diabase Dykes = 35.9ppb and Peat Bog = 99.6ppb

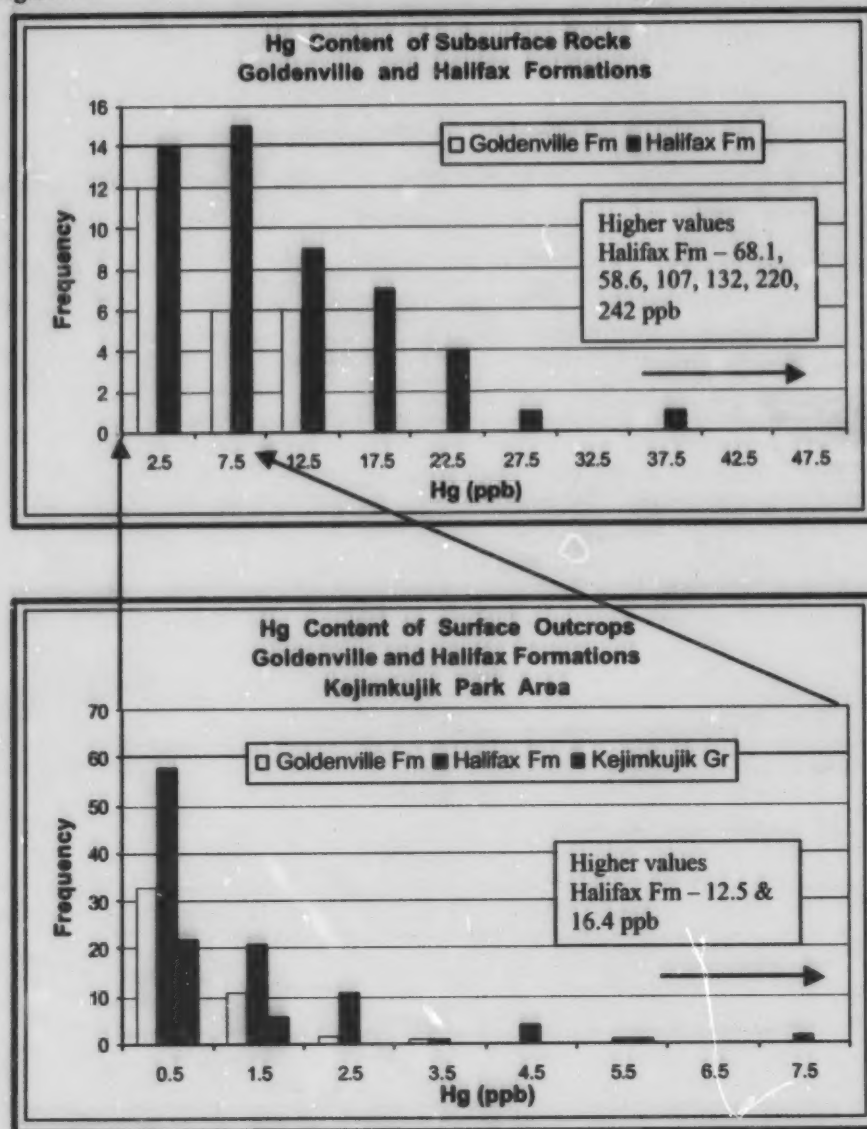
(Note: the peat bog material was collected outside the park near Paradise and the grey-green slate average is influenced by high values in the Digby area.

- The highest Hg value measured in the study thus far comes from black limestone in the eastern part of mainland Nova Scotia (well outside the park) and has a value of 386 ppb Hg.
- 3 till facies (slate, greywacke and granite) dominate local surficial geology

- Hg ranged from 6.4 ppb to 158.5 ppb (avg. 59.77 ppb, n=59, stats from 2000 field season, 2001 pending) Data is unique in the sense that, these are first Hg in till data available for this area. Hg values were not found to be significantly different from till in northern Nova Scotia.
- No discrete Hg source(s) (i.e. cinnabar-bearing veins) were identified. Interpreted correlation between increased Hg and geologic contacts
- Bedrock mapping/detailed magnetics indicate some geologic contacts on published geology maps require refining (i.e. Halifax/Goldenville contact south of the park is actually 500 m to 1000 m north of the contact shown on published maps), important for interpretation
- Geogenic mercury is added to surficial environments via major zones of tectonic activity via fault zones, subsurface hydrothermal activity and volcanoes. Modern examples include the Pacific Basin "Ring of Fire" and the volcanic/earthquake belt through southern Italy, Turkey and Iran. About 500 ma ago, a similar tectonic zone developed in what is now Appalachian North America. The Meguma Group metasedimentary rocks of eastern Nova Scotia, including Kejimikujik Park, were deposited during the early stages of this activity. The contained Halifax Formation black slates are a suitable candidate for the concentration of ambient aqueous and biogenic Hg at this time due to their elevated contents of organically derived carbon (to 2%) and contents of pyrite ( $\text{FeS}_2$ ) and pyrrhotite ( $\text{FeS}$ ) as high as 5%.
- Samples from surface exposures in the Park area contain very low Hg levels. Hg is lowest in rocks of the Goldenville Formation and Kejimikujik monzogranite, varying from <0.5 ppb to 4.0 ppb (n=47) and <0.5 to 5.8 ppb (n=31) respectively. Halifax slate samples are marginally higher at <0.5 to 16.4 ppb (n=100).
- Samples of Goldenville and Halifax formation lithologies from drill core contain substantially higher concentrations of Hg. Samples of Goldenville Formation core from Eastville, Wire lake and Molega Lake, Nova Scotia contain Hg from <0.5 to 13.4 ppb (n=35). Halifax Formation core from Clarksville, Eastville, and Lake Charlotte contain the highest Hg contents from <0.5 to 242 ppb (n=56). Some of the highest Hg analyses are related to traces of sphalerite  $[(\text{Zn},\text{Fe})\text{S}]$  at Eastville.
- The data may indicate that there is an incipient devolution of Hg from the bedrock surface during the earliest phases of weathering, thereby releasing Hg to soils, vegetation, water, and the atmosphere. The effect is most pronounced in sulphidic black slates which are more porous, have a well developed cleavage, and have a built in acid generation capacity with the presence of up to 5 percent pyrite and pyrrhotite. The data are not well constrained vis a vis mass balance considerations but certainly the observed Hg differential between surface and deeper bedrock have formed since the erosional event of the last glaciation the ended about 10,000 years ago. This data

indicates that surface rock samples may not provide an accurate measure of the trace Hg contents of bedrock.

Figure 7-1:



## 8. Soils

### 8.1 Sequential Analyses of Soil

*G. Hall, A. Rencz, and T. Goodwin*

#### Objective

- To investigate bioavailable forms of Hg in the soil column.

#### Methods

- Soils from 8 different locations (which spanned every major till type) were sampled.
- Samples were taken at 10-20 cm intervals to a depth of 1 metre.
- Sequential leaching of soils, applied to all humus and A-horizon soil samples from 2<sup>nd</sup> year sampling
- 0.1 M pyrophosphate to leach soil organics, 2 1-h leaches on 1 g of <180  $\mu$ m humus and <63  $\mu$ m A-horizon
- 0.25 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 0.25 M HCl, to leach amFeox, amAl<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>
- 1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% AcOH to leach cryFeox
- Aqua regia to leach residual organics, sulphides, some silicates and oxides
- All 5 leaches were analysed extensively by ICP-MS, CV-ICP-MS and ICP-ES

#### Results:

Figure 8-1:

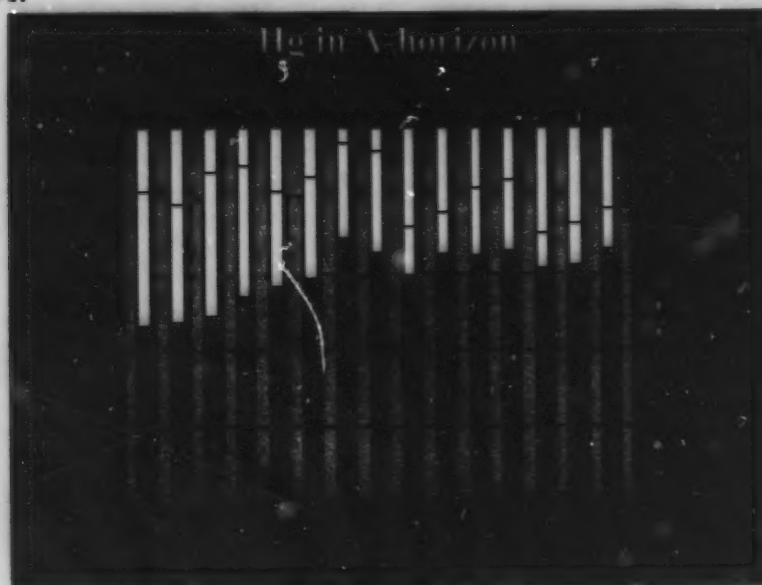
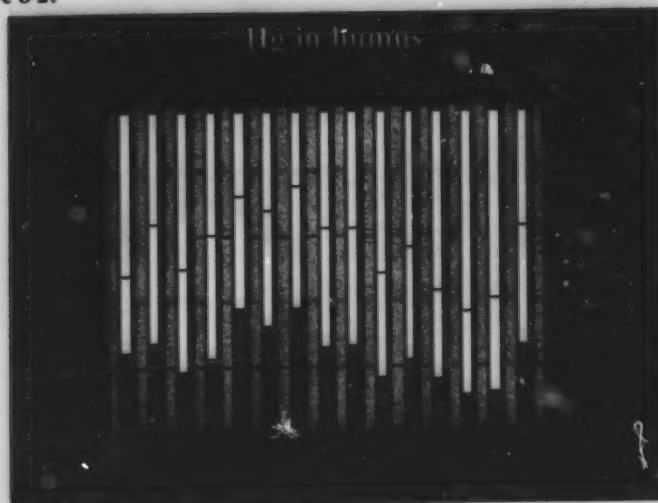


Figure 8-2:



- At these sites the percentage of organically bound Hg in the humus is apparently much *smaller* than that in the A-horizon below it, although the *absolute* amount of org-Hg is not and the total amount of Hg is also higher in the humus horizon. This is surprising if not suspicious
- The following slides of Pb indicate the expected: that the percentage of org-Pb in the humus dominates. Furthermore the behaviour of Al is as expected, org-Al being dominant in the humus and amFeox- associated Al (Alox) being dominant in the A-horizon

Figure 8-3:



**Figure 8-4:**

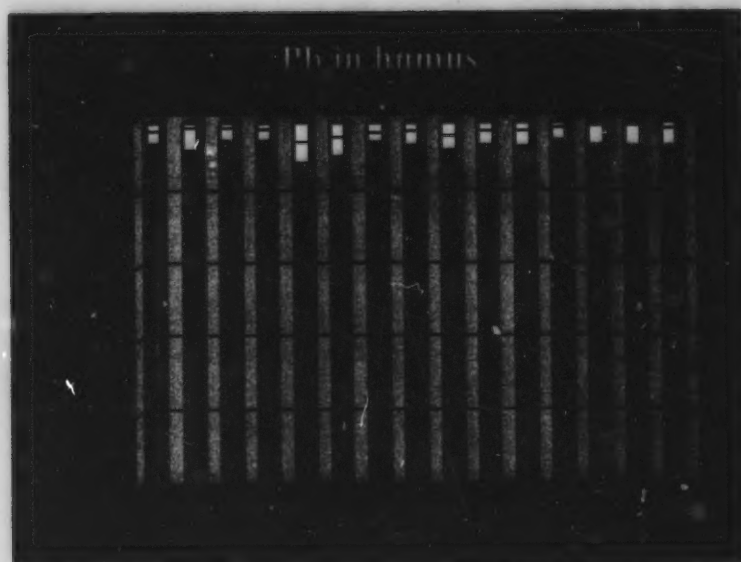


**Figure 8-5:**

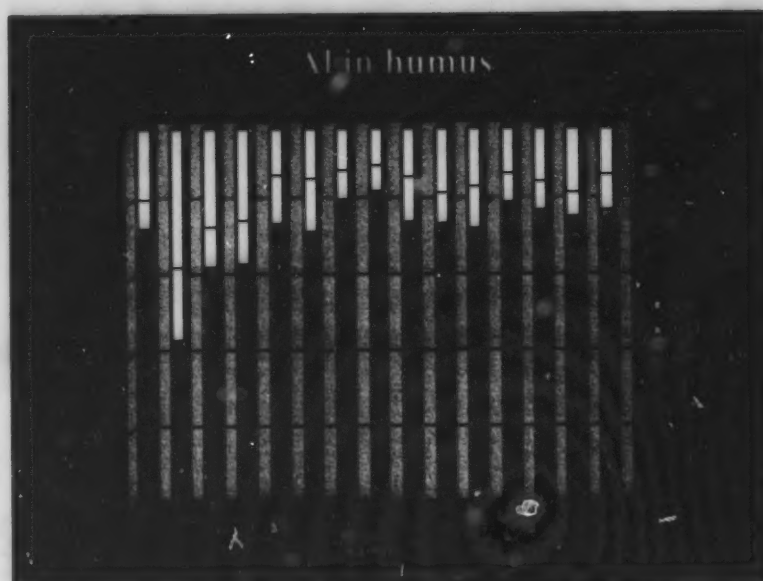


Figure 8-6:



- Therefore we decided to:
  - (1) Create various synthetic forms of Hg and verify where in the sequential extraction they were reporting. These forms include Hg,  $Hg_2Cl_2$ ,  $HgCl_2$ , HgO (2 forms), HgS (chemical), HgS (cinnabar), all mixed intimately and homogeneously in a granite (thoroughly tested, much work)
  - (2) Investigate whether we could differentiate residual tightly bound org-Hg (humins) and HgO from HgS in the final aqua regia digestion, to calculate *all* org-Hg

*Residual org-Hg and HgO from HgS*

- Approach was to use  $HNO_3$  to dissolve all forms of Hg prior to aqua regia (HgS)
- With various forms of Hg and controls in duplicate, studied 15, 30, 45, 60 and 75%  $HNO_3$  leaches and optimised digestion
- Then using HgO, HgS and cinnabar studied 20, 30, 40%  $HNO_3$  at different leach periods (1, 2, 3, 4 h)
- Optimum to isolate HgS from other forms is 40%  $HNO_3$ , 1 g, 2 h and then aqua regia (see following figures)

Figure 8-7:

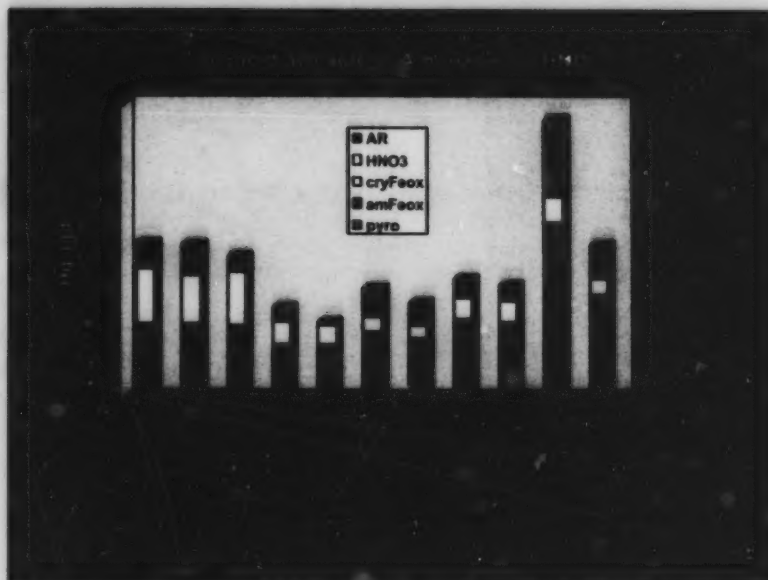


Figure 8-8

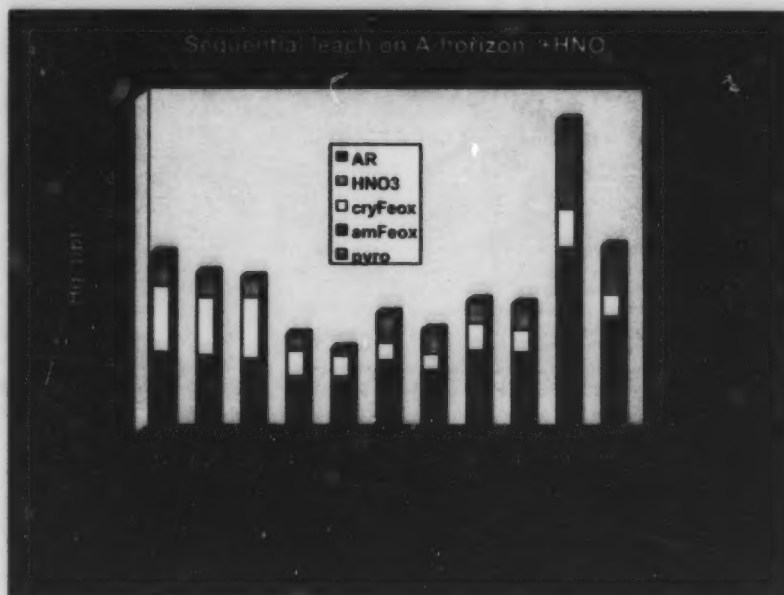


Figure 8-9:

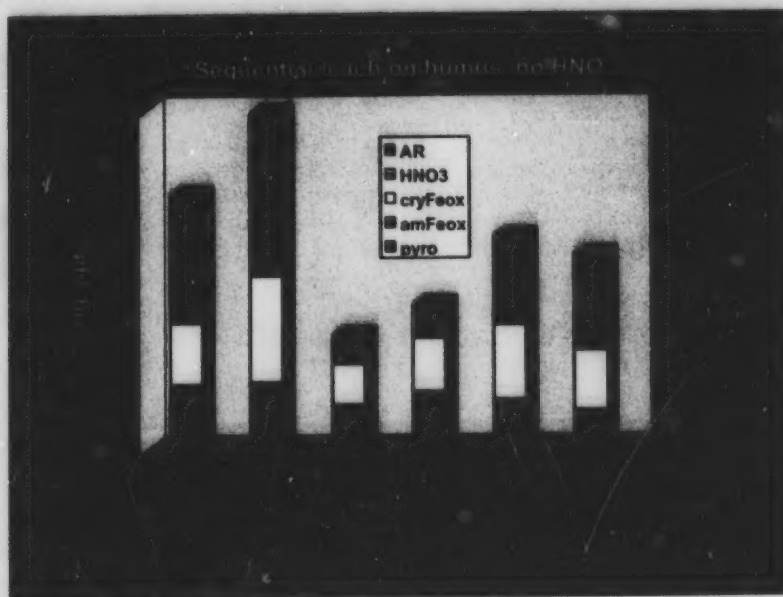
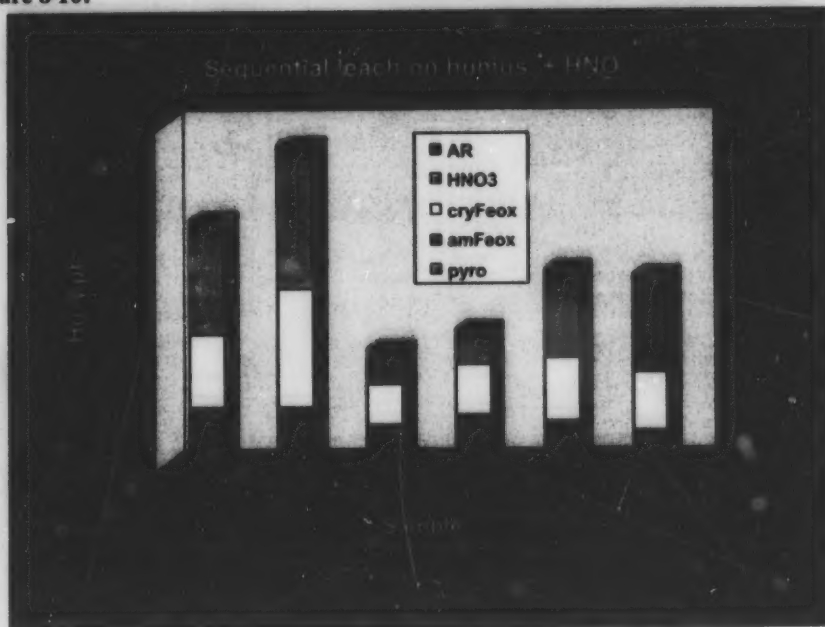


Figure 8-10:



*Sequential leach, analytical development*

- HgO forms are not completely dissolved with Feox phase prior to HNO<sub>3</sub>, need to modify hydroxylamine step
- • Require very weak leach prior to pyro to dissolve very loosely bound (available?) Hg, e.g. Ca(NO<sub>3</sub>)<sub>2</sub>, acetate but Hg is rapidly lost from typical weak leaches (spiking experiments performed)
- Previous schemes (literature) are in error as stability of Hg is overlooked, impacts severely on interpretations

*Sequential leach, application to soils*

- When new scheme is developed and proven, it will be applied to 10 vertical soil profiles collected at Keji
- Such data will then be interpreted to understand the cycling of Hg in the near subsurface, to identify dispersion in a vertical direction, sinks and sources

## 8.2 Mercury in Soil Gas

*A. Rencz, G. Hall, T. Goodwin, P. Rehn*

### Objective

- To determine if there is a naturally occurring geological source for the mercury
- To assess a relatively new mercury vapor flux sampling technique designed by Quicksilver Systems.

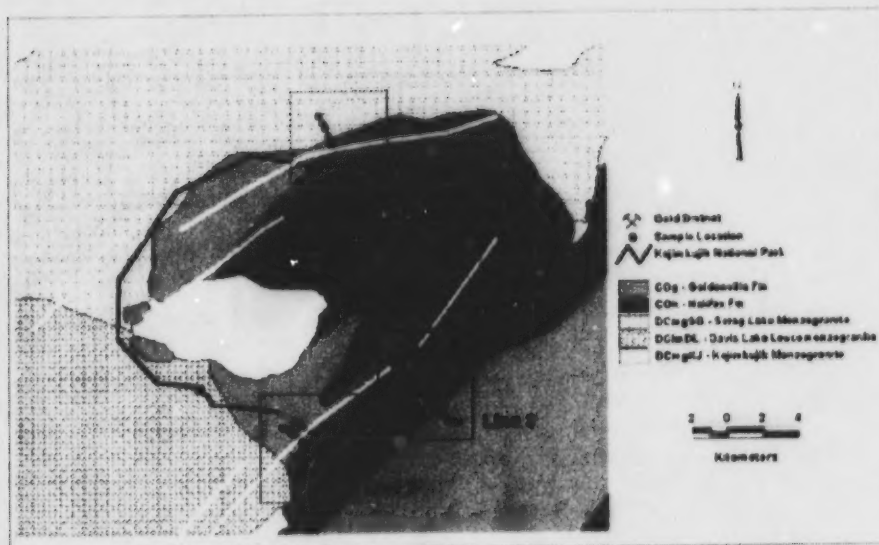
### Methods

- Various sample media including rock, soil, till, water, vegetation, and soil gas have been collected for Hg in and around the park.
- In September 2000, a total of 94 Quicksilver Hg vapor units were placed along four north-south trending lines around Kejimikujik National Park
- Line 1 was designed to: (1) cross the TSZ and a doubly plunging anticline, (2) to assess the presence of Au mineralization associated with the former West Caledonia Gold District, and (3) correlate Hg in soil gas results with till samples collected from the same sample site. The Hg vapor units were placed along a secondary dirt road at a sample spacing of 500 m.
- Line 2 was designed to: (1) cross two lithological units (Goldenville and Halifax formations) and (2) cross the TSZ. The Hg vapor units were placed along a logging road at variable sample spacings of 100 and 200 m.
- Line 3 was designed to: (1) cross two lithological units (Goldenville and Halifax formations), including the Goldenville-Halifax Transition Zone (GHTZ), (2) cross the TSZ, and (3) correlate Hg in soil gas results with till samples collected from the same sample site. The Hg vapor units were placed along a logging road at variable sample spacing of 100, 200, and 500 m.
- Line 4 was designed to: (1) cross three lithological units (Scrag Lake pluton, Goldenville Fm., and Halifax Fm.), (2) cross the EKSZ, and (3) to correlate Hg in soil gas results with till samples collected from the same sample site. The Hg vapor units were placed along Highway 8 at a sample spacing of 500 m.
- At each sample site, a 30 cm deep hole was dug by hand using a tree planter-style shovel. The units were assembled at each site and placed at the bottom of the hole. A silver strip collector was removed from an air-tight glass tube and inserted into a plastic mesh holder (Figure 4). A 20 cm by 20 cm piece of permeable fiberglass cloth (provided by Quicksilver Systems) was placed over the cup. The cloth created an air pocket below the unit and provides protection for the unit by reducing soil contact with the collector. Each site was marked with a picket and the sample location was

recorded by GPS (Garmin 12). The units were left buried and undisturbed for 30 days.

- After 30 days, the Hg collectors were carefully retrieved by digging up each unit. The silver strip collector was replaced into the air-tight glass tube. The air-tight tubes were immediately sent via courier to Quicksilver Systems in Bend, Oregon, for mercury analysis.
- At the laboratory, each silver strip was removed from the air-tight glass tube and sprayed with distilled water in order to rinse off any soil or organic particulate. The strips were dried with lint less paper and placed in a clean glass tube for analysis.
- The strips were heated to 700° C in a Thermolyne tube furnace, which forces Hg vapor into a stream of air. Mercury is then amalgamated onto a gold foil in a Jerome Gold Film Mercury Vapor Analyzer. Changes in the resistance of the gold foil compared to a reference gold foil represent the concentration of Hg (measured in nanograms). The lower and upper detection limits for the Jerome Vapor Analyzer are 0 ng and 100 ng, respectively.
- Certified reference standards are normally inserted with geochemical samples submitted for analysis in order to assess a laboratory's precision and accuracy. However, no known standards (apart from the previously mentioned reference gold foil) are known to exist for the Quicksilver Hg vapor units. Therefore, analytical control was limited to four randomly inserted "blank" Hg detection strips, that is, strips that were never buried. Eleven field duplicates, placed within 1-3 m of the original unit, were used to determine site variance.

**Figure 8-11:  
Results**



Based on the limited QC data (the four blanks and eleven field duplicates), the data is deemed to be of acceptable quality. All four blanks reported 0 ng Hg/strip and the results for field duplicates indicate the samples are representative of the area they were collected from.

- The minimum reported Hg in soil gas value is 0 ng Hg/strip and the maximum value is 78 ng Hg/strip ( $n = 94$ ,  $\bar{x} = 4.7$ ,  $sd = 9.3$ ). Based on a review of the data set using (1) a cumulative frequency plot, (2) rank and percentile, and (3) published results by Rehn and Rehn (1996), the authors have determined that background values for this study range from 0-6 ng Hg/strip and values  $\geq 7$  ng Hg/strip are considered anomalous. Apart from two highly anomalous values (46 and 78 ng Hg/strip) all values range between 0-15 ng Hg/strip. Results for lines 1-4 are presented in Figures 5a-d, respectively.
- **Line 1**  
The highest Hg in soil gas values (46 and 78 ng Hg/strip) reported for this study occur at the southern end of Line 1. The two consecutively spaced samples (500 m apart) are approximately 4 km northeast of known gold mineralization associated with the former West Caledonia Gold District. The district is characterized by a pair of doubly

plunging, northeast trending anticlines (Horne and Corey, 1994) and epithermal type textures (P. K. Smith, personal communications, August 9, 2000). The two anomalous sample sites are located on the inferred north edge of the TSZ.

- Line 2

Line 2 (Figure 5b) is characterized by eight anomalous sites (8-15 ng Hg/strip) that are flanked by at least two background values. This pattern was also noted by Rehn and Rehn (1996) across a drill inferred, deeply buried (up to 160 m of unconsolidated Quaternary overburden), gold ore body. The eight anomalous sites are spatially associated with the TSZ and the inferred structural contact between the Goldenville and Halifax formations.

- Line 3

Two single point anomalies (7 and 11 ng Hg/strip) were reported along Line 3 (Figure 5c), one at the north end of the line and one at the south end of the line. The northern anomalous sample site is spatially associated with the TSZ and the inferred structural contact between the Goldenville and Halifax formations. The southern anomalous sample site is spatially associated with the GHTZ.

- Line 4 There are no anomalous Hg in the soil gas values reported along Line 4 (Figure 5d).

- The data indicate there is a strong spatial relationship between inferred structures, namely the TSZ, and anomalous Hg in the overlying soil gas. Rehn and Rehn (1996) also noted a positive relationship between vertical structures and anomalous Hg in soil gas. The inferred trace of the EKSZ returned no anomalous Hg values in the soil gas. The lack of response may be a function of sample distribution, or an absence of Hg in the shear zone at this location. There also appears to be a positive relationship between Au mineralization in the West Caledonia Gold District and anomalous Hg in soil gas.
- Results from the 94 Hg vapour units indicate that several local geological sources of mercury (Hg) potentially exist in the vicinity of Kejimikujik National Park. These sources include inferred structures and the Goldenville - Halifax Transition Zone. Further, the Quicksilver Systems Hg vapour flux sampling unit is an effective sampling tool for detecting anomalous surface concentrations of Hg vapour produced by bedrock sources.

## 9. Vegetation

### 9.1 Modeling Net Mercury Uptake in Vegetation

*A. Rencz and N. J. O'Driscoll*

#### Objective

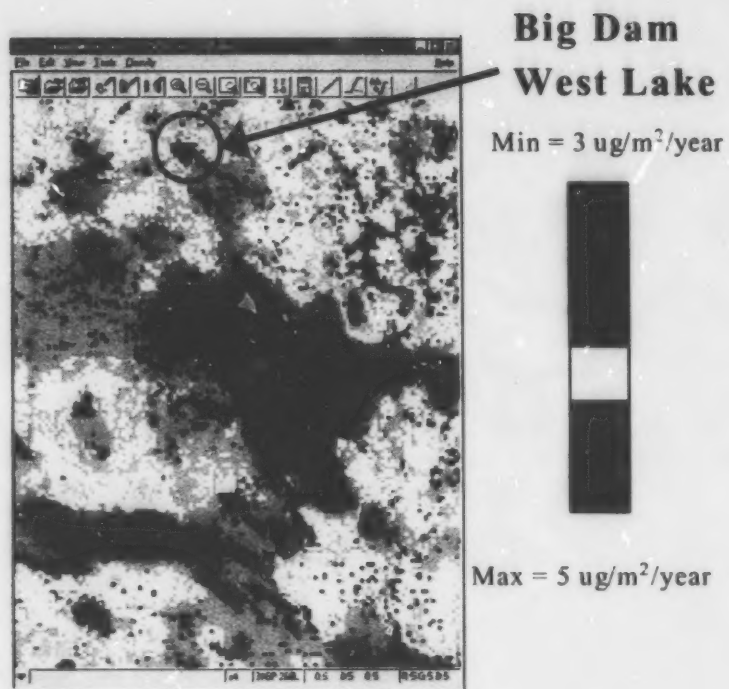
- To determine the average yearly flux of Hg from soil to vegetation

#### Methods

- Calculate the amount of Hg taken up by vegetation into the biomass.
- Using information from remote sensing determine the Net Primary Productivity (NPP) of the Big Dam West Lake (BDW) drainage basin
- Produce a map of the vegetation types within the BDW drainage basin.
- Determine an average concentration of Hg in biomass put on by each of the vegetation classes.

#### Results

- The amount of total mercury in NPP (terrestrial vegetation) within the BDW drainage basin ranges from  $3 \mu\text{g m}^{-2} \text{yr}^{-1}$  to  $5.2 \mu\text{g m}^{-2} \text{yr}^{-1}$ . Note that total input in precipitation is  $6.2 \mu\text{g m}^{-2} \text{yr}^{-1}$ .
- Over the entire basin the uptake in vegetation is 122.87 g
- Results of the net vegetation uptake calculation shown below. Results were generated using a combination of GIS and remote sensing imagery with vegetation sampling and analysis from the field sites. (Figure 9-1)



Net Mercury Accumulation in Vegetation (1 Year Average)

Figure 9-1: Net average mercury accumulation in vegetation over 1 year graphically represented using GIS

## 10. Remote Sensing

### 10.1 The Relationship of Spectral Properties and DOC in Lakes

A. Rencz and H. Hirtle

#### Objective

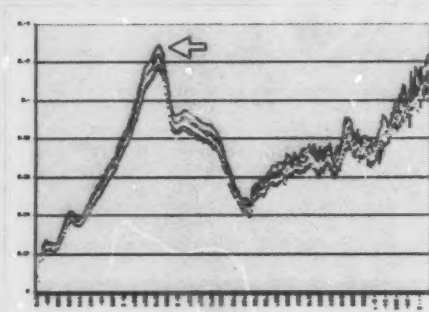
- To determine if spectral properties of lake water relate to DOC levels.

#### Methods

- Sampled 11 lakes for spectral measures, cations, mercury and DOC
- A field portable spectra radiometer (SE 590) was used to measure radiance at 50 cm above water for 252 wavelengths between 370 and 1132 nm. Ten spectral readings were taken at each site.
- Data was analyzed using simple linear regressions for each wavelength, and ratio of reflectance values for all combinations of 440nm, 670nm, 700nm, 520, 550, 395.5, 454.2, 576.3, 601.8 and 1127; multiple regressions were regressed against all possible ratio values

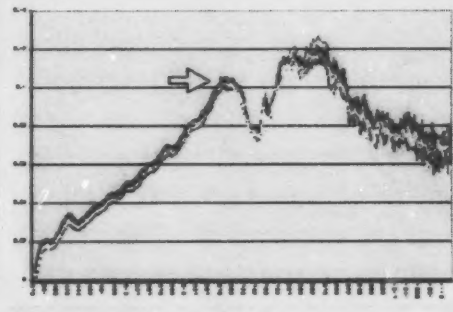
#### Results:

Figure 10-1:



Clear water lake- Cobrielle DOC=2.5ppm

Peak at 579.1 nm



Dark water lake- BDW - DOC=7.85

Peak at 695.8

#### Regression Results:

Highest single wavelength result: 576.3 nm  $R^2 = 0.855$  sig at .01

Highest single ratio result: 668.9/698.8  $R^2 = .877$  sig at .01  
698.8/668.8  $R^2 = .877$  sig at .01

#### Predictive Equations:

$$\text{Log DOC} = -1.319 - 10.919(\log R_{576.3} / \log R_{668.9}) + 13.039(\log R_{584.8} / \log R_{668.9})$$

- It is possible to use spectral readings to predict the level of DOC in lakes from Kejimikujik Park.

## 11. GIS

### 11.1 Modeling the DOC Content of Lakes

*A. Rencz*

#### Objective

- To develop a model to predict levels of DOC in Kejimikujik Park.

#### Methods

- Land cover classifications and remote sensing data were used to predict DOC concentrations

#### Results

- Using all of the variables to create a regression equation resulted in an equation with an adjusted  $r^2$  equal to 0.739, but a very high ratio of variables to cases (9:18). This method provides high predictive power but does not assist with explanation of the cause of variation in DOC concentrations.
- To assist with this explanation a stepwise regression was conducted. Three variables, flushing rate, area of deciduous forest and area of open land within the watershed, were included in the following equation.

$$\text{Log (DOC)} = 0.276 + 0.331 (\text{log Flushing}) - 0.029 (\text{log Open}) + 0.084 (\text{log Decid})$$

- This equation has an adjusted  $r^2$  value equal to 0.41 and tends to over predict DOC concentrations for lakes with low concentrations, such as Cobrielle Lake, and under predict concentrations for lakes with high actual concentrations, such as Big Red Lake.
- The flushing rate of a lake was found to be an important factor controlling the amount of DOC present within the lake through the identification of a positive correlation.
- A second variable positively correlated with DOC concentration is the area of deciduous forest that is located within the watershed of each lake.
- A third variable found to be responsible for increased DOC concentrations is the area of open land within the watershed of the lake
- Several authors have determined wetland area to be a major factor causing variation in DOC concentration. The presence of this type of land class in Kejimikujik is variable between watersheds but is in general quite low in all cases (i.e. less than 9 Ha). This may be due to the use of Landsat imagery for the classification of land cover types.

## 12. Mass Balance

### 12.1 A Multidisciplinary Mass Balance Model

*A. Rencz and N.J. O'Driscoll*

#### Objective

To contribute to a more complete understanding of the complex factors involved in mercury cycling in Kejimikujik Park, through:

- The creation of a conceptual model for both total and methyl mercury cycling within the Big Dam West Lake basin (See Figure 1)
- The creation of a mass balance model by the addition of quantitative mercury data to the various components of the conceptual model
- The comparison of mercury movement and residence time in the Kejimikujik mass balance model to mercury data from other ecosystems

#### Methods

- Nelson O'Driscoll to prepare a conceptual model of Hg cycling in Park. (Ph.D thesis)
- Nelson O'Driscoll to collate data from all collaborators to populate the conceptual model
- The research team has used a variety of methods since 1999 to measure the following: sedimentation, inflow and outflows, volatilization, atmospheric deposition, groundwater transport and bioaccumulation of mercury. Sampling included vegetation, water, sediment and soil and analysis by a variety of analytical methods (ICP-MS, CV-AAS, GC-AFS, Milestone Analysis, CV-AFS) and GIS applications (SPANS, PCI, Surfer).

#### Results:

- To date the model includes values for many of the boxes with in respect to total mercury.
- Will be able to provide more information on methyl mercury as analysis is completed this fall.
- Identified that the model is lacking important values for certain components: including vegetation volatilization and that more seasonal information is required.
- Although the calculations are still a work in progress, the current summary of major fluxes of total mercury to Big Dam West Basin are as follows:

Loss from Lake Basin

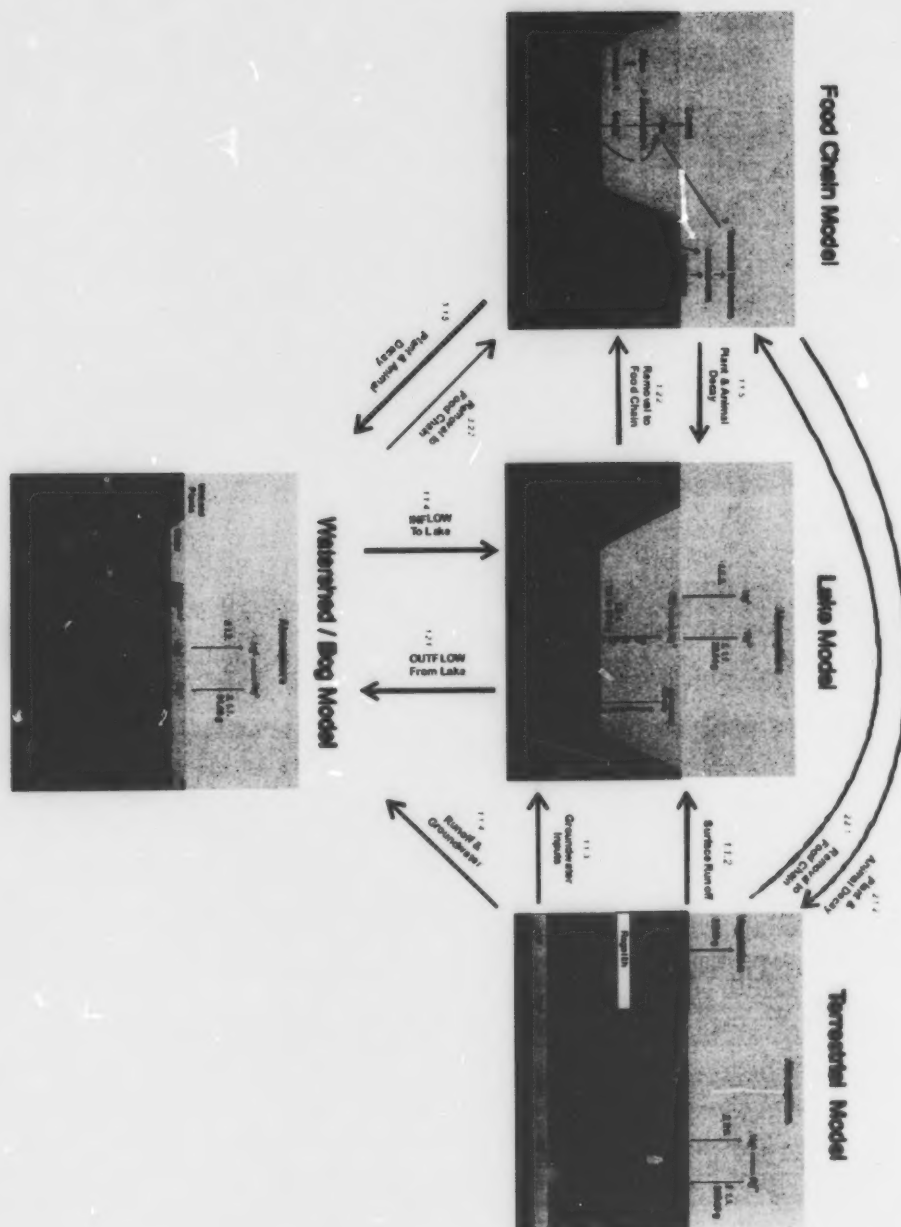
Sedimentation = 37.2 g  
Vegetation Uptake = 122.9 g  
Volatilization from Soil = 271.3  
Volatilization from Water = 17.0 g  
Outflow from Lake = 142.2 g  
Vegetation Volatilization = ?  
Other = ?  
SUM = 592.7 g

Input to Lake Basin

Groundwater = 52.0  
Other = ?  
Precipitation = 452.7 g  
SUM = 502.7

- Missing 90. g of mercury inputs to the lake basin using the current calculations. It should be noted that these are preliminary calculations and are subject to change as more data is available.

Figure 12-1:



### 13. Analytical Developments

#### 13.1 Mercury Stability and Sampling Methods

G. Hall

##### Objectives

- To examine sample preservation methods and sampling for mercury analysis

##### Methods

###### Water samples

- Since April analysed ca 210 for Hg, 70 also by ICP-MS and -ES and DOC
- Completed work on potential contamination in a variety of bottle types (poster at ICOBTE); paper in prep (poster information used)
- Carried out study of preservation of Hg in water with 3 concentrations of BrCl using 14 different Kejimikujik bulk water and control samples (spiked at +30 ppt Hg), all carried out in duplicate over a 28-day period (620 analyses). Study continuing to a longer time period

##### Results

- *Conclusions of Hg-in-water stability study (see five figures below)*
- Stability of Hg in water without an added preservative (BrCl) depends upon the amount of DOC present
- Samples with > ca 10 ppm DOC appear stable over 28 days without BrCl
- Samples with < ca 10 ppm DOC lose Hg to varying degrees but are stable in BrCl regardless of BrCl concentration (0.5-2 %)
- Proven that inexpensive HDPE or PP bottles may be used for water sampling without danger of contamination from the atmosphere on storage.
- Proven that the concentration of BrCl used to preserve Hg in solution is adequate at 0.5%; greater concentrations are not necessary for organic-rich surface waters. Indeed, such waters do not exhibit a stability problem in the absence of BrCl owing to complexation of Hg.
- Current selective leach extraction schemes are often in error for Hg as it is unstable in such dissolution media (e.g. little or no Hg found in very weak leaches, but Hg is unstable in such solutions). Hence, interpretation concerning the residence sites of Hg in soils and sediments, its bioavailability and mobility can be questionable. Sequential extraction scheme for soils and sediments with 6-7 multiple steps is being established.

Figure 13-1:

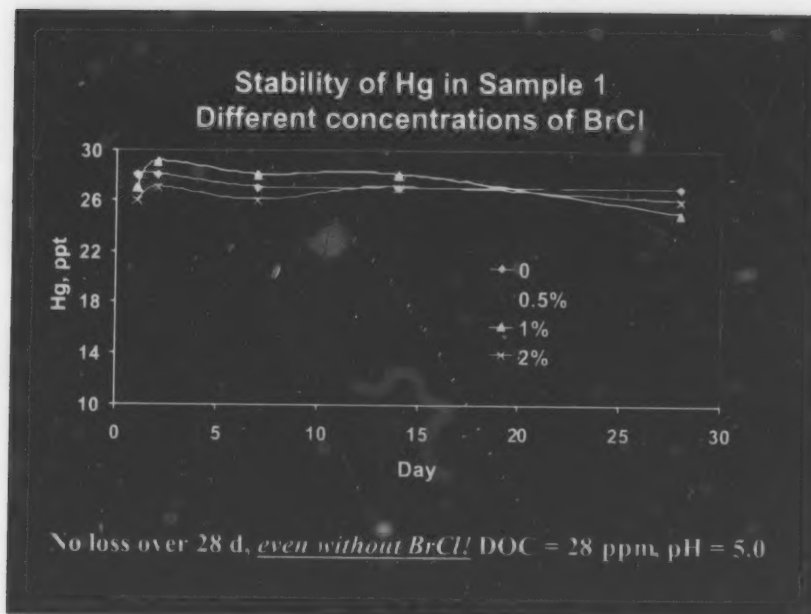
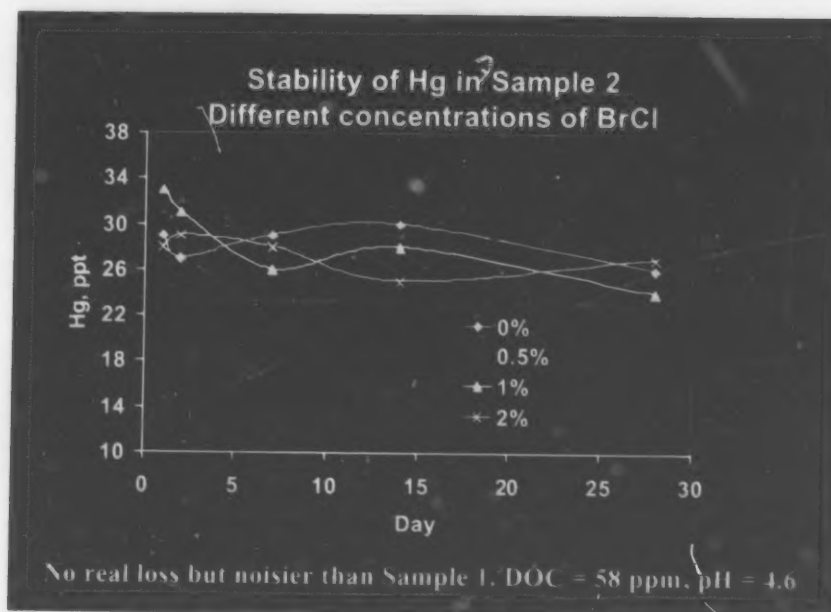


Figure 13-2:



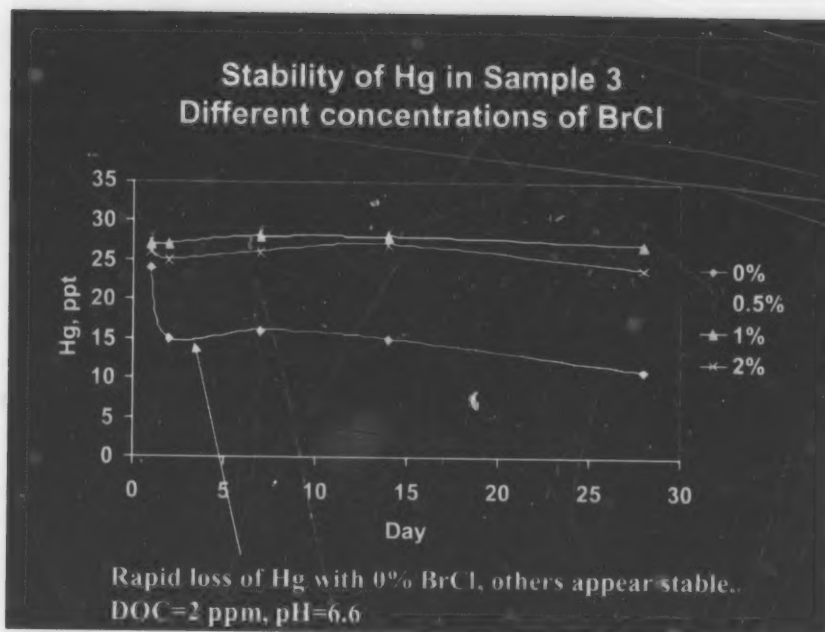


Figure 13-3 and 13-4:

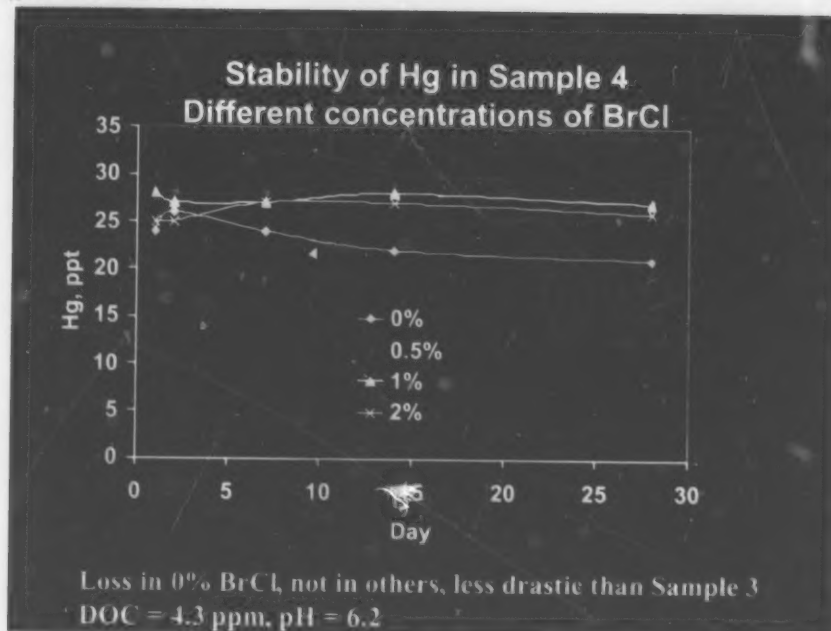
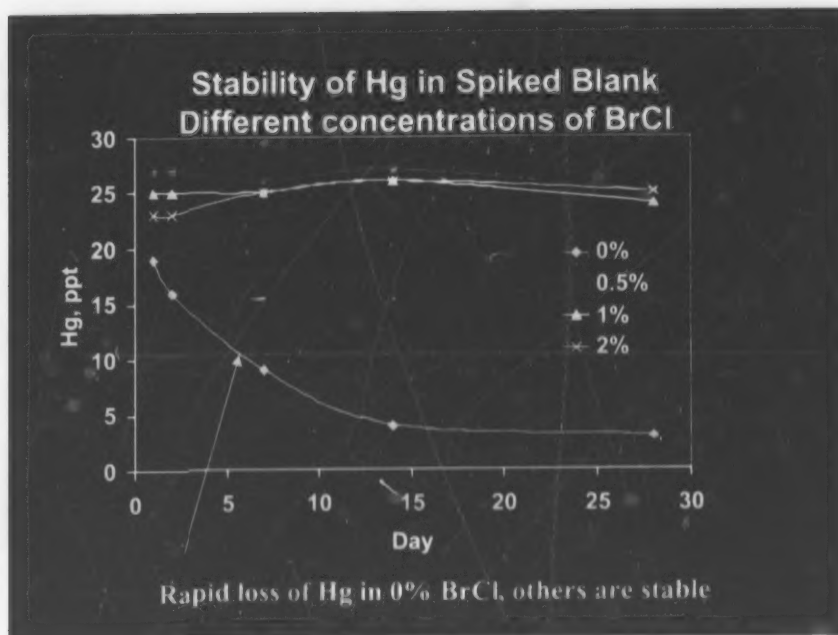


Figure 13-5:



#### 14. Future Mercury Research in Kejimikujik and Canada

D. Lean and A. Rencz, (with input from all members)

The mercury research in Kejimikujik Park was designed to determine why there is a mercury bioaccumulation problem in a remote area. There were several possible factors that may have contributed to this issue: 1) long range transport of mercury; 2) gold mining within the park; 3) uniqueness of the drainage basin (flatness resulting in a high percentage wetlands and high DOC export); 4) the fish grow slowly (accumulating years of mercury but still small enough for loons to eat). One of the big questions is, "Is the mercury in the park natural?" In most North American areas deposition is within a fairly narrow range 6-12 ug/m<sup>2</sup>/y and Kejimikujik Park is little different from other remote North American areas. There are currently several multi-million dollar mercury research projects ongoing in Canada, however some of the really important questions have not yet been answered. Some of the key areas that require more research are outlined below:

##### 1. Are deposition and volatilization in balance?

We only need re-volatilization of about 4 ng/m<sup>2</sup>/h over 8 hours for 200 days to completely account for all the release. Where do conditions exist where re-volatilization is low? Perhaps in a forest (if it is not blown off the top of the trees) it will accumulate (consistent with measurements of S. Beauchamp). But, what happens when trees are removed? As shown in the NCE Sustainable Forest Management Mercury study, when an area is logged, MeHg goes up in the downstream lakes. This may also be a problem in parts of Kejimikujik Park. Tree removal results in changes in the water table (similar to the effects of dam construction), and methyl mercury levels can be altered. We must also ask if the mercury is released from bare substrate as the sun shines on it and warms the soil or sand? Additional factors such as the moisture content of the soils must also be a factor.

##### 2. Is mercury that is deposited in sediments immobilized?

There are conditions where mercury is "irreversibly bound" by such chemicals as sulphides. Sulphides occur under extremely reducing conditions. There may be other chemicals that bind mercury and essentially take it out of the system. This is an area for investigation.

##### 3. When deposition occurs is mercury always exported or converted to MeHg?

This can occur if water is not exported and in areas where precipitation and water evaporation is in balance. One example is where once the forest soils retained moisture during the wet season and then it was used during the dry season. When the forest is thinned or removed there is more runoff during the wet season and the mosses and plants become desiccated so that during subsequent rain events the soils have lost the ability to retain water. The spring freshet, for example, becomes more severe and lasts for a shorter period of the time. It would also occur if a large part of the drainage basin is urbanized

(turned into parking lots). It is also known that during warmer-drier conditions there is less DOC exported. This should result in less mercury being exported.

4. After clear cutting is there greater export of DOC from the drainage basins and how does this affect the mercury cycle?

With higher DOC there is usually more mercury released. With clear cutting, the bogs become flushed faster leaving them drier during the summer period. The delicate balance which results in sulphide accumulation is critical. If conditions are right for methyl mercury formation then with the early fall rains mercury export from the bogs will occur.

5. Has Hg deposition increased?

While mercury deposition in Kejimikujik is not unusually high in comparison to other remote sites, it still may have increased over time. We have seen in other areas that conditions can change or the deposition rate can be high and there is still no methyl mercury formed. In Kejimikujik the conditions are right for MeHg formation so any increase in deposition will result in an increase in MeHg. When this increase exceeds the ability of the system to remove MeHg then it will accumulate and become a problem.

6. Has hydrology changed?

Draining wetlands has been a priority for many farmers and other settlers. This has been particularly true for sphagnum bogs. Instead of water falling on waterlogged soils and running directly off again (changed little from the rainwater itself), it now flows through the soil profile and becomes very coloured. By flowing through the soils rather than over the soils, the water carries away mercury that has accumulated over many years.

7. Where are the sites of mercury methylation?

It would seem that the source of the methyl mercury is in the wetlands. However this is difficult to quantify and it is not clear as to the actual site of methylation (possibly the interface between mineral and organic sediments in the wetlands). It is well known that when reservoirs are first constructed whether it is a beaver pond or a hydroelectric generating station, mercury accumulates. The common explanation is that the flooding has resulted in increased microbial activity creating the appropriate conditions for MeHg production. An alternative hypothesis is that with dam construction, the water becomes more turbid. Consequently, photoreduction will be less. The same amount of mercury comes in but less gets out so there is more available for methylation. What is often overlooked is the surface-to-volume ration is decreased. The surface area is a factor in photoreduction and volatilization whereas the volume is related to depth and depth is a factor in controlling oxygen levels.

8. Are there seasonal effects?

There is considerable variation over the year with respect to methyl mercury in the various pools. Further work is needed to quantify the levels of methylation and demethylation in the various pools over the entire season.

9. Is Kejimikujik representative of other freshwater sites?

If a model to predict Hg levels in fish is done can the model be exported to other areas with similar results.

10. How does vegetation affect the mercury cycle?

Results suggest the importance of vegetation in the cycling of mercury. However it is difficult to quantify the total impact of vegetation in terms of uptake from the soil, uptake/release from the atmosphere and return to the system via litter fall and stem flow.

These are just a few of the on-going questions to be answered. The Kejimikujik project has given us a unique look into a remote freshwater environment that has developed a mercury problem due to environmental characteristics. The importance of, geology, precipitation and the transportation and transformation of mercury is currently being assessed through mass balance work.

## 15. List of Products

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## 16. Researchers Associated / Students Trained

| Student                | Degree | Affiliation         | Collaborator       | Position    | Affiliation         |
|------------------------|--------|---------------------|--------------------|-------------|---------------------|
| Ken Griffiths          | BSc    | Acadia U.           | Dr. Cindy Stacer   | Prof.       | Dalhousie U         |
| Carrie-Ellen Gabrielle | BSc    | Dalhousie U         | Dr. Colin Bell     | Prof.       | Acadia U.           |
| Harry Berley           | BSc    | Ottawa U            | Dr. Mark Hines     | Prof.       | Alaska U.           |
| Elizabeth Mader        | BSc    | Ottawa U            | Dr. Paul Arn       | Prof.       | New Brunswick U.    |
| Tanya Peron            | BSc    | Victoria U.         | Dr. Fan Rui Meng   | Prof.       | New Brunswick U.    |
| Belinda Culgen         | BSc    | Ottawa U            | Dr. Michelle Robin | Prof.       | Ottawa U            |
| Huda Yusuf             | BSc    | Ottawa U            | Dr. D. Fortin      | Prof.       | Ottawa U            |
| Paul Ferguson          | BSc    | Acadia U.           | Steven Siciliano   | PDF         | Ottawa U            |
| Susan Winch            | MSc    | Ottawa U            | Chris Daughney     | PDF         | Ottawa U            |
| Heather Hirtle         | MSc    | Carleton U.         | Geoff Howell       | Res. Assoc. | Nova Scotia Nat Res |
| Krista Page            | MSc    | Dalhousie U         | Reid Harris        | Res. Assoc. | Tetra Tech          |
| Lisa Van Loon          | MSc    | Ottawa U            | Terry Goodwin      | Res. Assoc. | Nova Scotia Nat Res |
| Michelle Watson        | MSc    | Victoria U.         | Bob Nickel         | Res. Assoc. | Acadia U.           |
| A.M. O'Beirne-Ryan     | PhD    | Nova Scotia Nat Res | Patty Rehn         | Res. Assoc. | Quicksilver         |
| Jonathan Holmes        | PhD    | Ottawa U            | Rob Tordon         | Res. Assoc. | Environment Canada  |
| Nelson O'Driscoll      | PhD    | Ottawa U            | Todd Smith         | Res. Assoc. | Environment Canada  |
| Valbonna Cello         | PhD    | Ottawa U            | Pierre Pelchat     | Res. Assoc. | NRCan               |
|                        |        |                     | J.P. Rioux         | Res. Assoc. | Ottawa U            |
|                        |        |                     | Melissa Lagrande   | Res. Assoc. | Ottawa U            |

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